Scope and Limitations of Fulvene Syntheses. Preparation of 6-Vinyl-Substituted and -Functionalized Fulvenes. First Examples of Nucleophilic Substitution on a 6-(Chloromethyl)fulvene†

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Received September 13, 1994®

Very few 6-vinylfulvenes have previously been reported in the literature. In a few cases where Little's procedure (using pyrrolidine as base) has been employed, most enones undergo conjugate attack by the cyclopentadienyl anion followed by either a retroaldol reaction or dihydropentalene formation. In several cases, Diels–Alder reaction of the enone with cyclopentadiene occurs rather than condensation. We have found that in cases where the Little procedure fails to give the desired 6-vinylfulvenes, the Thiele method using NaOH (or NaOMe in some cases) as base gives satisfactory results. In the latter instances, Michael attack is completely suppressed in all but one example. By appropriate choice of base, a variety of fulvenes carrying functional groups on the 6-alkyl position can be prepared. Some of these fulvenes have been shown to undergo further functional group transformations (e.g., nucleophilic substitutions), giving rise to derivatives bearing SR, S(O)R, N_3, or SCN groups.

Introduction

The chemistry of pentafulvenes[1] has been a subject of great interest theoretically and because these compounds exhibit diverse modes of cycloadditions.[2] Suitably substituted fulvenes have systematically been employed in organic synthesis using mainly three different approaches: (a) Little's diyl trapping experiments involving fulvene-derived bicyclic azo compounds;[3] (b) intramolecular cycloaddition of fulvenes containing various olefinic groups on the exocyclic double bond;[4] (c) decomposition of saturated bicyclic fulvene endoperoxides as precursors of allene oxides/cyclopropanones carrying a carbonyl functionality on the side chain (Figure 1).[5]

The classical approach[6] to fulvenes involves the condensation of a carbonyl compound with cyclopentadiene[7] using pyrrolidine as base in methanol solvent, which seems to be the most efficient in terms of generality and yield. It appears that there are mainly three limitations of the latter method: (a) Michael addition of the base when there is an α,β-unsaturated carbonyl group present in the fulvene. This side-reaction has been ameliorated by the authors to some extent by substituting pyrrolidine by diethylamine. (b) Sterically hindered carbonyl compounds, in particular, aromatic ketones, cannot be converted to the corresponding fulvenes by this method. Little suggests that an iminium ion intermediate between pyrrolidine and the carbonyl group precedes the attack by the cyclopentadienide anion; sterically hindered ketones, not being able to form the iminium ion readily, are less reactive under these conditions. The use of a stronger base, e.g., OH^- or RO^- does yield the desired fulvenes in such cases.[8] (c) Under Little's conditions certain α,β-unsaturated carbonyl compounds that are also reactive dienophiles (e.g., acrolein and methyl vinyl ketone) undergo Diels–Alder reactions with cyclopentadiene rather than yield 6-vinylfulvenes.[9] Sterically hindered α,β-unsaturated ketones, on the other hand, suffer conjugate attack by the cyclopentadienide anion, rather than addition to the carbonyl group. Mesityl

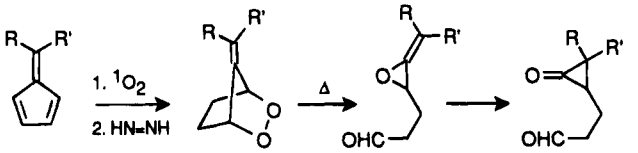


Figure 1.

† Dedicated to Professor Wolfgang Lüttke, Georg-August University Göttingen, on the occasion of his 75th birthday.

‡ On leave from the Shanghai University of Science and Technology.

® Abstract published in *Advance ACS Abstracts,* February 1, 1995.

(1) For reviews, see: (a) Yates, P. *Advanced Alicyclic Chemistry*; Academic Press: New York, 1968; Vol. 2, p 59–184. (b) Bergman, E. D. *Chem. Rev.* **1968**, *68*, 41–84. (c) Day, J. H. *Chem. Rev.* **1953**, *53*, 167–189. (d) Zeller, K. P. Pentafulvenes. In *Methoden der Organischen Chemie;* 1985; Vol.5/2C, pp 504–684. (e) Neuenschwander, M. Fulvenes. In *The Chemistry of Double-Bonded Functional Groups*; Patai, S., Ed.; John Wiley: New York, 1989; pp 1131–1268.

(2) (a) Fleming, I. *Frontier Orbitals and Organic Chemical Reactions:* John Wiley & Sons: New York, 1985; p 178–81; (b) Houk, K. N. in *Pericyclic Reactions*; Academic Press: New York, 1977; Vol. 2, pp 238–39.

(3) For reviews, see: (a) Little, R. D. *Chem. Rev.* **1986**, *86*, 875–884. (b) Little, R. D.; Masjedizadeh, M. R.; Moeller, K. D.; Dannecker-Doerig, I. *Synlett* **1992**, 107.

(4) (a) Kaiser, R.; Hafner, K. *Angew. Chem. Int. Ed. Engl.* **1970**, *9*, 892. (b) Kaiser, R. and Hafner, K. *Angew. Chem. Int. Ed. Engl.* **1973**, *12*, 335. (c) Wu, T.-C.; Houk, K. N. *J. Am. Chem. Soc.* **1985**, *107*, 5308, and references cited therein. (d) Gupta, Y. N.; Patterson, R. T.; Bimanand, A. Z.; Houk, K. N. *Tetrahedron Lett.* **1986**, *27*, 295. (e) Dunn, L. C.; Houk, K. N. *Tetrahedron Lett.* **1978**, 3411. (f) Gajewski, J. J.; Cavender, C. J. *Tetrahedron Lett.* **1971**, 1057. (g) Trost, B. M.; Melvin, L. S., Jr. *Tetrahedron Lett.* **1975**, 2675.

(5) (a) Erden, I.; Amputch, M. *Tetrahedron Lett.* **1987**, *28*, 3779. (b) Erden, I.; Drummond, J.; Alstad, R.; Xu, F.-P. *Tetrahedron Lett.* **1993**, *34*, 1255. (c) Erden, I.; Drummond, J.; Alstad, R.; Xu, F.-P. *Tetrahedron Lett.* **1993**, *34*, 2291. (d) Erden, I.; Xu, F.-P.; Drummond, J.; Alstad, R. *J. Org. Chem.* **1993**, *58*, 3611.

(6) (a) Thiele, J. *Chem. Ber.* **1900**, *33*, 666. (b) Thiele, J. *Justus Liebigs Ann. Chem.* **1906**, *348*, 1. (c) Freiesleben, W. *Angew. Chem.* **1963**, *75*, 576. (d) Kerber, R. C.; Linde, H. G., Jr. *J. Org. Chem.* **1966**, *31*, 4321. (e) Olah, G. A.; Surya Prakash, G. K.; Liang, G. *J. Org. Chem.* **1977**, *42*, 661. (f) Hanack, M.; Eggensperger, H. *Justus Liebigs Ann. Chem.* **1963**, *31*, 663.

(7) Stone, K. J.; Little, R. D. *J. Org. Chem.* **1984**, *49*, 1849.

(8) (a) Kice, J. L.; Parham, F. M. *J. Am. Chem. Soc.* **1958**, *80*, 3792. (b) NaH has also been used as base for fulvene formation: Sternbach, D.; Hughes, J. W.; Burdi, D. F. *J. Org. Chem.* **1984**, *49*, 201. (c) With sterically hindered cyclic 1,3-dicarbonyl compounds, CpLi (cyclopentadienyllithium) and CpMgBr have been used: Jacobs, S. J.; Schulz, S. A.; Javin, R.; Novak, J.; Dougherty, D. A. *J. Am. Chem. Soc.* **1993**, *115*, 1744.

0022-3263/95/1960-0813$09.00/0

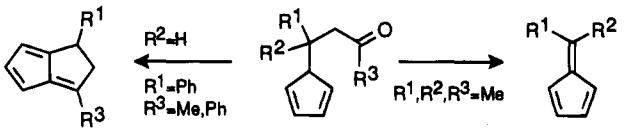


Figure 2.

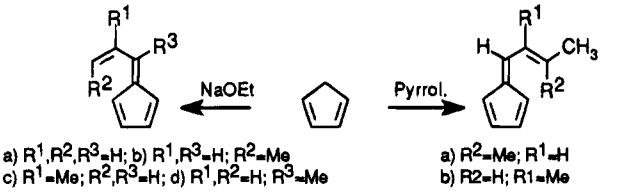


Figure 3.

oxide, for instance, gives rise to 6,6-dimethylfulvene. Benzalacetone and benzalacetophenone likewise undergo initial Michael attack, followed by intramolecular fulvene formation yielding the corresponding 1,2-dihydropentalenes.[9]

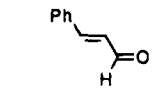
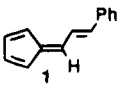
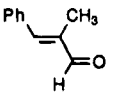
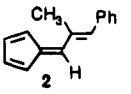
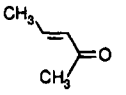
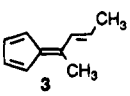
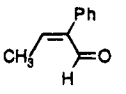
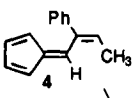
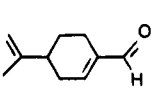
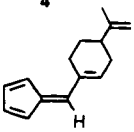
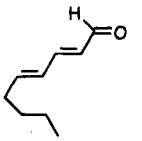
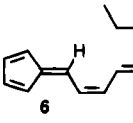
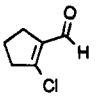
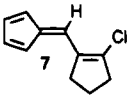
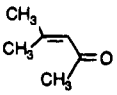
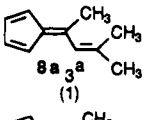
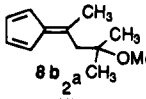
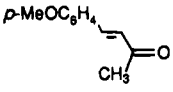
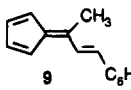
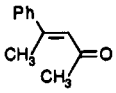
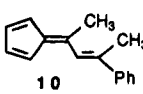
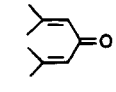
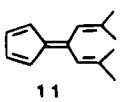
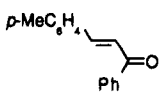
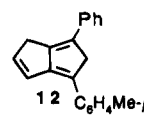
Four aliphatic 6-vinylfulvenes have been synthesized by Neuenschwander et al.,[10] albeit in very low yields (0.5–22.7%), using the classical Thiele procedure[6] (NaOR base). Griesbeck[9] recently applied Little's method to the synthesis of two aliphatic vinylfulvenes. He reported, however, that 1- or 4-aryl-substituted enones under the same conditions underwent Michael attack leading mainly to 1,2-dihydropentalenes.

In conjunction with our "fulvene endoperoxides–allene oxide/cyclopropanone" project[5] we needed a variety of 6-vinyl- and other substituted fulvenes carrying functional groups on the exocyclic double bond. We found that both Little's and Thiele's methods complement each other for the synthesis of vinylfulvenes. We further found that 1,2-dihydropentalene formation from most enones constitutes an exception rather than a rule when the "right conditions" are applied. Moreover, we report here the synthesis of a number of functionalized fulvenes and some transformation reactions thereof.

Results and Discussion

(a) Mesityl Oxide and Phorone (Table 1, 8a, 8b, 11). Fenton and Hurwitz[11] reported the reaction of mesityl oxide with cyclopentadiene and NaOH in methanol to give a compound in 60% yield, the structure of which was tentatively assigned to that of the vinylfulvene based on analytical data. The formation of undisclosed amounts of "Thiele's ether"[12] and a "methyl ether" (both of unknown structure at the time) were also mentioned. In our hands, this reaction gave rise to three products under the same conditions (43% total yield), 6,6-dimethylfulvene, **8a**, and **8b** in a 2:1:1 ratio, respectively (Table 1). These were readily separated from one another by chromatography on SiO_2 and characterized by spectroscopic and analytical methods. The starting ketone presumably underwent a conjugate attack by methanol to some extent prior to or after fulvene formation. The best yields of **8a** and **8b** were obtained when the condensation was carried out with sodium methoxide in methanol. A 94% yield of a 3:1 mixture of **8a** and **8b**

Table 1. Synthesis of 6-Vinylfulvenes

Carbonyl Comp.	Base	Fulvene	Yield
	Pyrrol.	 **1**	62%
	Pyrrol.	 **2**	77%
	Pyrrol.	 **3**	53%
	Pyrrol.	 **4**	83%
	Pyrrol.	 **5**	97%
	Pyrrol.	 **6**	41%
	Pyrrol.	 **7**	64%
	NaOMe (NaOH)	 **8a** $_3^a$ (1)  **8b** $_2^a$ (1)	94% (43%)
	NaOH	 **9**	71%
	NaOH	 **10**	67%
	NaOH	 **11**	73%
	NaOMe	 **12**	85%

[a] The numbers refer to relative ratios of **8a** and **8b**

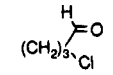
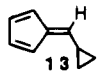
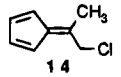
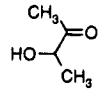
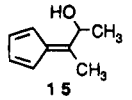
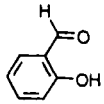
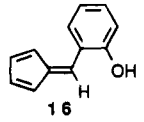
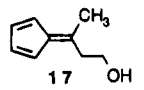
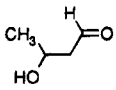
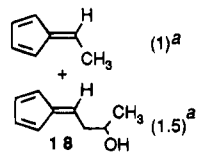
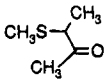
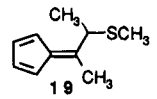
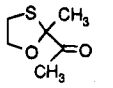
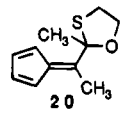
(9) Griesbeck, A. G. *J. Org. Chem.* **1989**, *54*, 4981. *Chem. Ber.* **1990**, *123*, 549.

(10) (a) Neuenschwander, M.; Meuche, D.; Schaltegger, H. *Helv. Chim. Acta* **1963**, *46*, 1760; **1964**, *47*, 1022. (b) See also: Kohler, E. P.; Kable, J. *J. Am. Chem. Soc.* **1934**, *56*, 2756. (c) For the syntheses of a number of fulvenes and 6-(2-chloro-and -acetoxyvinyl)fulvenes from 1-chloroalkyl acetates and 3-chloro- or -acetoxy-2-propenals and cyclopentadiene, see Neuenschwander, M.; Iseli, R. *Helv. Chim. Acta* **1977**, *60*, 1061. (d) Schaltegger, H.; Neuenschwander, M.; Meuche, D. *Helv. Chim. Acta* **1965**, *48*, 955. (e) Kyburz, R.; Schaltegger, H.; Neuenschwander, M. *Helv. Chim. Acta* **1971**, *54*, 1037. (f) Hoffmann, H. M. R.; Koch, O. *J. Org. Chem.* **1986**, *51*, 2939.

(11) Fenton, D. M.; Hurwitz, M. J. *J. Org. Chem.* **1963**, *28*, 1646.

(12) The structure of Thiele's ether has been elucidated as 2-(1-methoxy-1-methylethyl)-6,6-dimethylfulvene: Shamma, M.; Gianannetti, J. P.; Henry, R. B.; Melbardi, A. *Tetrahedron* **1963**, *19*, 1409.

Table 2. Functionalized Fulvenes

Carbonyl Comp.	Base	Fulvene	Yield
	Pyrrol.	 13	74%
	Pyrrol.	 14	66%
	Pyrrol.	 15	85%
	Pyrrol.	 16	92%
	Pyrrol.	 17	64%
	Pyrrol.	 18 (1)[a] + (1.5)[a]	68%
	Pyrrol.	 19	81%
	NaOMe	 20	76%

[a] The numbers in parentheses refer to relative ratios

were isolated from this reaction. Under these conditions 6,6-dimethylfulvene formation was completely suppressed.

Mesityl oxide and phorone gave under Little's conditions exclusively 6,6-dimethylfulvene. On the other hand, phorone reacted with cyclopentadiene in MeOH using NaOH to furnish the 6,6-divinylfulvene **11** in 73% yield. Clearly, the method of choice for the preparation of 6-vinylfulvenes is the NaOH (or NaOMe in two cases)/MeOH procedure when the starting enone is prone to Michael attack.

(b) α,β-Unsaturated Carbonyl Compounds (Table 1, 1–12). Application of Little's procedure to α,β-unsaturated aldehydes and sterically less hindered enones (e.g., 3-penten-2-one) gave the corresponding 6-vinylfulvenes in 41–97% yields, respectively, without any traces of 1,2- or 1,5-dihydropentalenes. By contrast, the pyrrolidine method cannot be applied to various enones for the synthesis of 6-vinylfulvenes. We found that in those cases where conjugate addition dominates, leading to dihydropentalenes, the use of NaOH instead of pyrrolidine in methanol effectively circumvents this problem. Only in the case of methoxychalcone, dihydropentalene **12** still was formed, regardless of the base used.

(c) Chlorocarbonyl Compounds (Table 2, 13, 14).

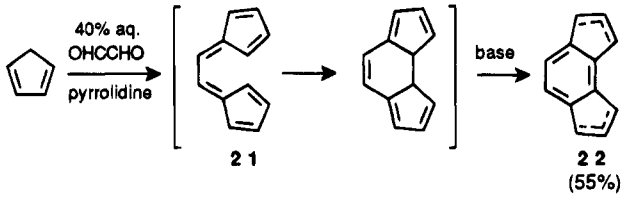


Figure 4.

α-Chloroacetone gave, using pyrrolidine, the corresponding fulvene **14** without a side reaction (e.g., displacement of chloride by the oxygen in the initial 1,2-adduct might have been envisioned). When 4-chlorobutanal was used, 6-cyclopropylfulvene (**13**) was the sole product. Here, pyrrolidine affects 1,3-dehydrochlorination either before or after fulvene formation. This approach represents the most convenient synthesis of **13** from a readily available starting compound; the preparation of cyclopropane carboxaldehyde thus is unnecessary.[13a,b]

(d) 3-Hydroxycarbonyl Compounds (Aldols) (Table 2, 17, 18). 4-Hydroxy-2-butanone gave (pyrrolidine base) the corresponding fulvene **17** in 64% yield. 3-Hydroxybutanal under the same conditions led to a mixture of the corresponding fulvene **18** and 6-methylfulvene in 41 and 27% yields, respectively.[14] 4-Hydroxy-3-methyl-2-butanone and diacetone alcohol, on the other hand, gave only 6-ethyl-6-methylfulvene and 6,6-dimethylfulvene, respectively. The following conclusions may be drawn from these results: sterically encumbered β-hydroxycarbonyl compounds are more reluctant to form the iminium ion than their counterparts that are less hindered at the carbonyl group; thus retrogression efficiently competes with fulvene formation. An electronic factor may be superimposed on the steric factor, in particular, in regard to 4-hydroxy-2-butanone and 3-hydroxybutanal: the rate of the reverse aldol reaction increases with increasing stability of the carbonyl fragments.[15,16]

(e) α-Hydroxycarbonyl Compounds (Table 2, 15). 3-Hydroxy-2-butanone gave in excellent yield the corresponding fulvene **15**, using pyrrolidine as base. Even though an 85% aqueous solution of starting ketone was used, the presence of a substantial amount of water did not hamper the reaction whatsoever.

(f) Dicarbonyl Compounds.[17] When 40% aqueous glyoxal was treated with cyclopentadiene in methanol in the presence of pyrrolidine, the product isolated from this reaction by silica gel chromatography in 55% yield) proved to be a mixture of isomeric dihydro-*as*-indacenes

(13) (a) The preparation of 6-cyclopropylfulvene (**13**) from cyclopropane carboxaldehyde and cyclopentadiene in the presence of pyrrolidine has been mentioned, but neither the yield nor spectral data of it have been reported: Griesbeck, A. G. *J. Prakt. Chem.* **1992**, *334*, 558. (b) When the reaction was terminated at an earlier stage, ~5% of 6-(3-chloropropyl)fulvene was detected in the GCMS analysis of the product mixture. MS 156/154 ((M + 2)/M$^+$: 3:1), 105, 92, 91, 65, 39.

(14) 6-Methylfulvene: (a) Thiec, J.; Wiemann, J. *Bull. Soc. Chim. Fr.* **1957**, 366. (b) Freiesleben, W. *German Patent* **1963**, 1, 146,050; *Chem. Abstr.* **1963**, *59*, 9914. (c) Hafner, K.; Hafner, K. H.; König, C.; Kreuder, M.; Ploss, G.; Schulz, G.; Sturm, E.; Vöpel, K. H. *Angew. Chem.* **1963**, *75*, 35. (d) Sturm, E.; Hafner, K. *Angew. Chem.* **1964**, *76*, 862.

(15) (a) Noyce, D. S.; Pryor, W. A. *J. Am. Chem. Soc.* **1959**, *81*, 618. (b) Noyce, D. S.; Snyder, L. R. *J. Am. Chem. Soc.* **1959**, *81*, 620. (c) Noyce, D. S.; Reed, W. L. *J. Am. Chem. Soc.* **1959**, *81*, 624.

(16) (a) Stiles, M.; Wolf, D.; Hudson, G. V. *J. Am. Chem. Soc.* **1959**, *81*, 628. (b) Jensen, J. L.; Hashtroudi, H. *J. Org. Chem.* **1976**, *41*, 3299.

(17) The syntheses of dipentafulvenes derived from 1,*n*-dicarbonyl compounds ($n > 3$) have been accomplished using Little's procedure: Erickson, M. S.; Cronan, J. M., Jr.; Gabrile Garcia, J.; McLaughlin, M. L. *J. Org. Chem.* **1992**, *57*, 2504.

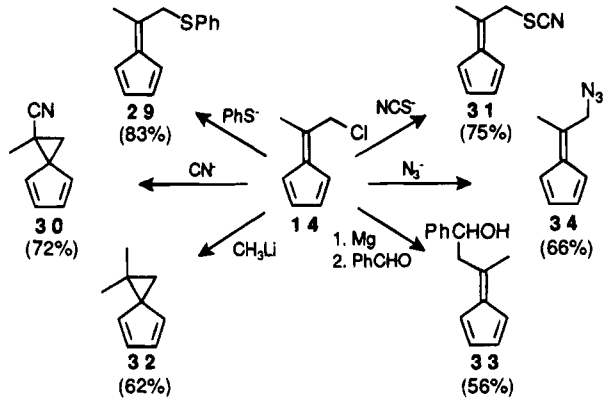
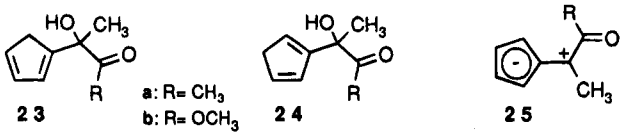


Figure 5.

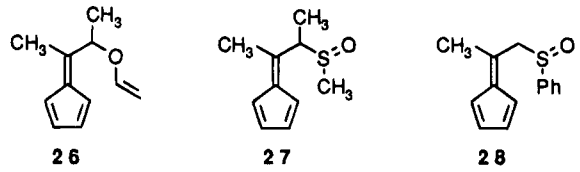
(**22**),[18b,19] as an NMR analysis clearly showed (Figure 4). Previously, Sauter and Prinzbach[19] reported the formation of **22** in 3–5% yield from the condensation of glyoxal sulfate with cyclopentadienylsodium. They were able to detect the 1,2-bis(cyclopentadienyl)ethane (**21**) intermediate at low temperatures by spectroscopy. The method described herein appears to be the most efficient approach to **22**.

In an attempt to prepare a 6-acyl substituted fulvene we treated 2,3-butanedione with cyclopentadiene in the presence of pyrrolidine. In this reaction, the desired fulvene did not form; instead, a mixture of the cyclopentadienes **23a** and **24a** was isolated. Methyl pyruvate likewise gave a mixture of the isomers **23b** and **24b** under the same conditions. These results suggest that 6-acylfulvenes are difficult to form. The initial adducts are reluctant to undergo dehydration and isomerize to the α-hydroxcarbonyl substituted cyclopentadienes instead. The reluctance of the addition products **23** and **24** to undergo dehydration may be attributed to the fact that polarization of the π-electrons of the exocyclic double bond toward the ring, a general characteristic of fulvenes,[1a] would render the corresponding resonance structure **25** (positive charge on C6, α to the carbonyl) considerably less stable than the alkyl substituted analogs.



Reactions of Functionalized Fulvenes

(a) To study sigmatropic shifts of cyclopropanones derived from fulvene endoperoxides we needed 6-(1-vinyloxy)-substituted fulvenes. Toward that end fulvene **15** (note Table 2) was subjected to a $Hg(OAc)_2$-catalyzed transetherification with ethyl vinyl ether. The reaction proceeded without any side reaction to give the desired vinyl ether **26** in 68% yield. In connection with the same study 6-thioalkyl and sulfoxyalkyl- or aryl-substituted fulvenes were required. We were able to prepare these compounds by two different approaches. The first of these involves fulvene formation from an α-thioalkyl substituted carbonyl compound followed by $NaIO_4$ oxidation of the thioether to the sulfoxide; 6-[1-(methylthio)-ethyl]fulvene (**19**) (Table 2) and the corresponding sulfoxide **27** were prepared by this protocol in 81 and 78% yields, respectively. An attempt to condense (methylsulfinyl)propanone ($CH_3SOCH_2COCH_3$) with cyclopentadiene in the presence of base did not lead to fulvene formation, presumably due to the acidity of the α-hydrogen at the sulfinyl carbon, leading to enolate formation, and deactivation of the carbonyl as an electrophile. The second method whereby **28** has been prepared involves a nucleophilic displacement of chloride in **14** (Table 2) by PhS^-, followed by $NaIO_4$ oxidation of the phenylthio group in **29**, as described below.



(b) 6-(Chloromethyl)-6-methylfulvene (**14**) was employed in a variety of transformations summarized in Figure 5: nucleophilic displacement by PhS^-, SCN^-, and N_3^- all gave the corresponding fulvenes **29**, **31**, and **34**, respectively. The CN^- ion, on the other hand, underwent initial conjugate attack at C6, leading to the spiro[2.4]-heptadiene derivative **30**. A similar result was obtained upon treatment of **14** with methyllithium, giving rise to the known spiro[2.4]heptadiene[20] **32**. Chlorofulvene **14** also served as an excellent precursor of the corresponding Grignard reagent; upon quenching with benzaldehyde, alcohol **33**[21a] was obtained in 56% yield. The present approach is a convenient alternative to the deprotonation of 6-alkylfulvenes with lithium diisopropylamide (LDA) at −78 °C.[21a,b] Although we have not explored condensations of the aforementioned Grignard reagent with other electrophiles, it is likely that a variety of fulvenes bearing useful functionality should become available from **14** and its analogs (Figure 5).

Conclusions

We have evaluated two existing methods for fulvene synthesis. The first employs pyrrolidine as base for the condensation of an aldehyde or ketone with cyclopentadiene; the second, being the classical Thiele procedure, utilizes either hydroxide or alkoxide as base. We found that for aldehydes in general and for most dialkyl ketones the best variant is the former method. Pyrrolidine not only acts as base, it also appears to catalyze the addition step by forming an iminium ion, thus rendering the carbonyl carbon more electrophilic ($k_2 > k_{-2}$). In addition, the elimination step efficiently competes with the fragmentation to the reactants ($k_e > k_{-2}$). The lack of reactivity of sterically hindered and aromatic ketones under Little's conditions may be attributed to two fac-

(18) (a) Rapoport, H.; Smolinsky, G. *J. Am. Chem. Soc.* **1960**, *82*, 1171. (b) Katz, T. J.; Balogh, V.; Schulman, J. *J. Am. Chem. Soc.* **1968**, *90*, 734. (c) Battiste, M. A.; Timberlake, J. F. *J. Org. Chem.* **1977**, *42*, 176.

(19) (a) Prinzbach, H.; Sauter, H. *Angew. Chem. Int. Ed. Engl.* **1972**, *11*, 296. (b) *Chem. Ber.* **1977**, *110*, 1382.

(20) (a) Schröder, W.-D.; Friedrichsen, W. *Justus Liebigs Ann. Chem.* **1978**, 1648. (b) Nishida, S.; Asanuma, N.; Murakami, M.; Tsuji, T.; Imai, T. *J. Org. Chem.* **1992**, *57*, 4658. (c) For additions of organometallic reagents to C6 of fulvenes, see: Ziegler, K; Schäfer, W. *Justus Liebigs Ann. Chem.* **1934**, *511*, 101. (d) For addition of chlorocarbene to the exocyclic double bond of fulvenes, see: Amaro, A; Grohmann, K. *J. Am. Chem. Soc.* **1975**, *97*, 3830. (e) Conjugate addition of lithium dimethylcuprate to 6-(3-oxobutanyl)fulvene has been utilized in the synthesis of spirovetivanes by Buchi et al.: Buchi, G.; Berthet, D.; Decorzant, R.; Grieder, A.; Hauser, A. *J. Org. Chem.* **1976**, *41*, 3208.

(21) (a) Nyström, J.-E.; Byström, S. E.; Ristola, T.; Ekström, J. *Tetrahedron Lett.* **1988**, *29*, 4997. (b) Hine, J.; Knight, D. B. *J. Org. Chem.* **1970**, *35*, 3946.

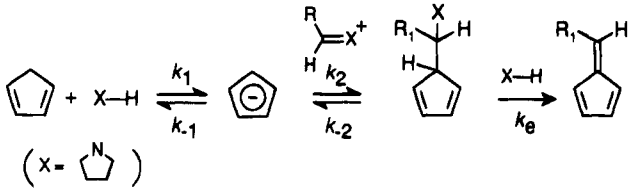


Figure 6.

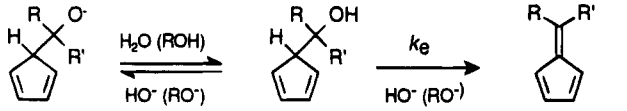


Figure 7.

tors: (a) the carbonyl group is too unreactive or sterically too hindered to form the iminium ion; thus the addition process is too slow; (b) the elimination step becomes the rate-determining step. The relatively weak base strength of pyrrolidine [pK_a(pyrrolidine-H^+) = 11.27][22] causes the cleavage step compete efficiently with the elimination step ($k_{-2} > k_e$) (Figure 6).

The use of a stronger base such as HO^- [pK_a (H_2O) = 15.7][23] or RO^- [pK_a(ROH) ≈ 17–20][23,24] enhances the rate of the dehydration step ($k_e > k_{-2}$); thus fulvene formation prevails (Figure 7).

While a variety of vinylfulvenes are readily accessible by Little's procedure (see Table 1), certain sterically hindered α,β-unsaturated ketones are attacked by the cyclopentadienyl anion in a Michael fashion, either leading to 1,2-dihydropentalenes, or fulvenes derived from the condensation of cyclopentadiene with the retroaldol product. These latter pathways can be circumvented by using NaOH instead of pyrrolidine in those cases (except for chalcone). The competing reactions when an enone is condensed with cyclopentadiene are summarized in Figure 8.

1,2-Addition to the carbonyl group can occur with either base. With the weaker base pyrrolidine, k_{-2} is expected to dominate elimination ($k_{-2} > k_e$), since proton abstraction from the OH group will be favored versus C–H abstraction from the cyclopentadiene. The alternative pathway, i.e., conjugate addition to the enone, will then compete. The relative acidities of a carbonyl α-hydrogen ($pK_a \approx 19–20$)[25] and the cyclopentadienyl C–H ($pK_a \approx 16$)[26] will now become the product-determining factors ($k_5 > k_{-4}$). Once the cyclopentadienyl anion is formed, either intramolecular attack on the carbonyl group will occur, leading to the 1,2-dihydropentalenes (the dominant mode), or a retroaldol reaction will take place, giving rise to the respective dialkyl fulvene (as in the case of mesityl oxide). When the stronger base (OH^- or RO^-) is used, the 1,2-addition pathway will become predominant, leading to the 6-vinylfulvene ($k_e > k_{-2}$).

Using Little's procedure, carbonyl compounds bearing functional groups, such as Cl or OH, can be converted to fulvenes without side reactions (Table 2, compounds **14**–**20**). When the chloro group is at the γ-position of the carbonyl group, as in 4-chlorobutanal, intramolecular displacement of the halide occurs, giving 6-cyclopropylfulvene (**13**). We found that Little's procedure tolerates aqueous solutions of carbonyl compounds; fulvene **15** and dihydro-*as*-indacenes (**22**) were prepared in 85 and 55% yields, respectively, using aqueous solutions of 3-hydroxy-2-butanone and glyoxal. Moreover, the work described herein unveiled a new facet of fulvene reactivities: these compounds tolerate a variety of reaction conditions at the 6-alkyl group, such as Lewis-acid-catalyzed transetherification, oxidation, nucleophilic substitutions, or carbanion formation in the form of a Grignard reagent.

Experimental Section

General. ^1H NMR (300 MHz) and ^{13}C NMR (75 MHz) spectra were recorded on a GE QE-300 spectrometer with $CDCl_3$ or $(CD_3)_2CO$ as the solvent and TMS as internal standard. IR spectra were run on a Nicolet 550 FT-IR spectrometer, GCMS data were obtained using a Hewlett-Packard 5890A GC (equipped with a 25 m × 0.2 mm cross-linked methyl silicone column, helium carrier gas) linked to a Model 5971A EIMS. Column chromatographic separations were carried out with Davison silica gel (grade 62, 60 × 200 mesh), and Merck silica gel (grade 60 PF_{254}) was used for preparative TLC. Pyrrolidine was freshly distilled before use. All reactions were conducted under an atmosphere of dry nitrogen or argon. For the preparation of the fulvenes by Little's procedure, see ref 7. All yields reported in this study are averages of at least two trials. The procedure for the preparation of **8a,b** is representative of the ones used for the other fulvenes listed in Table 1 (NaOH/MeOH). Due to their thermal lability and propensity to polymerize as well as their sensitivity to oxygen, the fulvenes prepared in this study were not sent out for elemental analysis. The purity of each product was >95%, as determined by a combination of GC/MS, ^1H, and ^{13}C NMR spectroscopy. Melting points are uncorrected.

Procedure for the Synthesis of 8. (a) The Sodium Hydroxide Method. To 7.84 g (0.08 mol) of mesityl oxide were added 5.3 g (0.08 mol) of freshly distilled cyclopentadiene and 20 mL of methanol containing 1.2 g (0.03 mol) of sodium hydroxide. The solution was stirred under nitrogen, heated to 60 °C, and maintained at this temperature for 2 h. The reaction mixture was then acidified with 1 mL of glacial acetic acid. The mixture was diluted with 100 mL of ether, the layers were separated, and the ethereal layer was washed with water (2 × 30 mL). The organic layer was dried over $MgSO_4$ and concentrated in vacuo at 0 °C, and the products were separated by column chromatography on silica gel eluting with petroleum ether. Three compounds were isolated in a combined yield of 43%. The major component (50%) was 6,6-dimethylfulvene, in addition to **8a** (25%) and 6-methyl-6-(2-methoxy-2-methylpropyl)fulvene (**8b**) (25%). The spectra of **8a** and **8b** are listed below in the Experimental Section.

(b) The Sodium Methoxide Method. To 1.2 g (0.02 mol) of sodium methoxide in 15 mL of methanol were added at 0 °C 1.2 mL (0.015 mol) of freshly distilled cyclopentadiene, followed by 1.96 g (0.02 mol) of mesityl oxide. The mixture was stirred at room temperature for 2 h, acidified with 1.5 g of acetic acid, and diluted with 50 mL of water, and the product was extracted with ether (2 × 50 mL). After the removal of solvent in vacuo the residue was subjected to column chromatography on SiO_2, eluting with petroleum ether. The first fraction, 1.23 g (8.42 mmol, 56% yield), was identified as 6-methyl-6-(2-methyl-1-propenyl)fulvene (**8a**). The second fraction, 1.01 g (5.67 mmol, 38% yield), proved to be 6-methyl-6-(2-methoxy-2-methylpropyl)fulvene (**8b**).

6-(2-Phenylethenyl)fulvene (1) (62%, pyrrolidine): mp 73–75 °C; ^1H NMR (300 MHz, $CDCl_3$/TMS) δ 7.60–7.25 (m, 6H); 6.95 (d, J = 9.9 Hz, 1H); 6.94 (d, J = 15.9 Hz, 1H); 6.65 (m, 1H); 6.59 (m, 1H); 6.50 (m, 1H); 6.27 (dt, J = 5.1, 1.8 Hz, 1H) ppm; MS m/z 180 (M^+), 127, 89.

6-(1-Methyl-2-phenylethenyl)fulvene (2): mp 67–68 °C (77%, pyrrolidine); ^1H NMR (300 MHz, $CDCl_3$/TMS) δ 7.42–

(22) (a) Cabani, S.; Conti, G.; Lepori, L. *Ric. Sci.* **1968**, *38*, 1039. *J. Chem. Soc., Faraday Trans.* **1971**, *67*, 1933. (b) *Handbook of Tables for Organic Compound Identification*, 3rd ed.; Rappoport, Z., Ed.; CRC Press: Cleveland, OH, 1976. (c) Perrin, D. D. *Dissociation Constants of Organic Bases in Aqueous Solution*; Butterworths: London, 1965.
(23) Murto, J. *Acta Chem. Scand.* **1964**, *18*, 1043.
(24) Ballinger, P.; Long, F. A. *J. Am. Chem. Soc.* **1959**, *81*, 1050.
(25) Chiang, Y.; Kresge, A. J.; Tang, Y. S.; Wirz, J. *J. Am. Chem. Soc.* **1984**, *106*, 460.
(26) Streitwieser, A., Jr.; Nebenzahl, L. L. *J. Am. Chem. Soc.* **1976**, *98*, 2188.

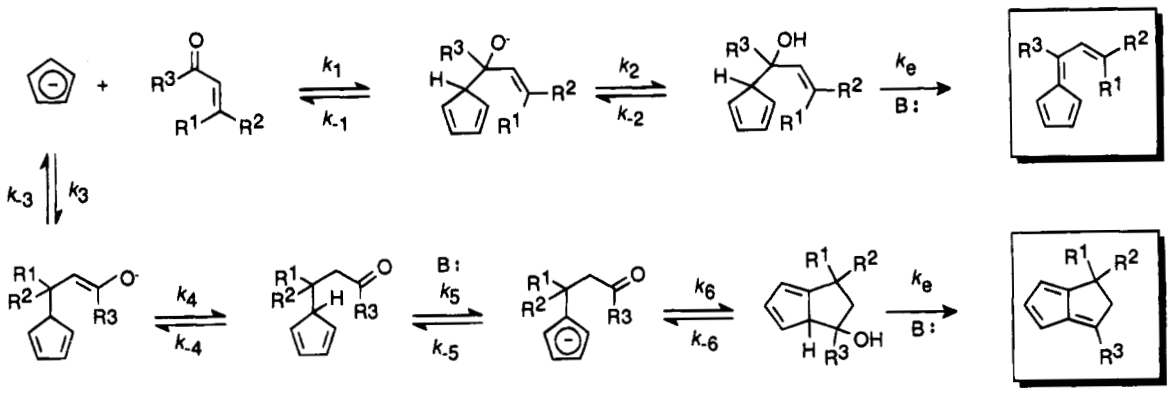


Figure 8.

7.24 (m, 5H); 6.99 (s, 1H); 6.97 (s, 1H); 6.74 (m, 1H); 6.38 (m, 1H); 6.48 (m, 1H); 6.30 (m, 1H); 2.34 (s, 3H) ppm; MS *m/z* 194 (M^+), 117, 115, 91, 39.

6-Methyl-6-(1-propenyl)fulvene (3) (53%): ^{1}H NMR (300 MHz, $CDCl_3$/TMS) δ 6.9 (dq, 15.3, 1.5 Hz, 1H); 6.66 (ddd, J = 4.5, 2.1 Hz, 1H); 6.575 (ddd, J = 4.5, 2.1 Hz, 1H); 6.50 (m, 2H), 6.23 (dq, J = 15.4, 6.9 Hz, 1H); 2.26 (s, 3H); 1.94 (dd, J = 6.9, 1.5 Hz, 3H) ppm; MS *m/z* 132 (M^+), 117, 115, 91, 39.

6-(1-Phenyl-1-propenyl)fulvene (4) (83%): ^{1}H NMR (300 MHz, $CDCl_3$/TMS) δ 7.1–7.45 (m, 5H); 6.95 (s, 1H); 6.42 (q, J = 7.23 Hz, 1H); 6.28 (m, 2H); 6.18 (m, 2H); 1.67 (d, J = 7.23 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$/TMS) δ 143.7, 143.5, 142.6, 139.6, 134.1, 133.6, 131.4, 130.2, 130.1, 129.2, 128.2, 120.8, 23.3 ppm; MS *m/z* 194 (M^+), 179, 165, 115, 88, 40.

6-(4-Isopropenyl-1-cyclohexenyl)fulvene (5) (97%): ^{1}H NMR (300 MHz, $CDCl_3$/TMS) δ 6.8 (s, 1H); 6.65 (m, 1H); 6.59 (m, 1H); 6.44 (m, 1H); 6.32 (m, 1H); 6.25 (m, 1H); 4.77 (narrow m, 1H); 4.75 (s, 1H); 1.77 (s, 3H); 2.8–1.4 (m, 7H) ppm; MS *m/z* 198 (M^+), 183, 155, 130, 77.

6-(1,3-Octadienyl)fulvene (6) (41%): ^{1}H NMR (300 MHz, $CDCl_3$/TMS) δ 6.85–6.1 (m, 7H); 6.0 (m, 1H); 5.46 (m, 1H); 2.2 (m, 2H); 1.4 (m, 4H); 0.9 (t, 7.2, 3H) ppm; MS *m/z* 186 (M^+), 157, 143, 129, 128, 115, 91, 77, 41, 39.

6-(2-Chlorocyclopenten-1-yl)fulvene (7) (64%, pyrrolidine): ^{1}H NMR ($CDCl_3$/TMS) δ 7.15 (s, 1H); 6.6 (m, 1H); 6.5 (m, 1H); 6.47 (m, 1H); 6.3 (m, 1H); 2.88 (t, J = 7.5 Hz, 2H); 2.75 (t, J = 7.5 Hz, 2H); 2.07 (quintet, J = 7.5 Hz, 2H); ^{13}C NMR ($CDCl_3$/TMS) δ 145.6, 142.8, 136.1, 135, 131.3, 130.1, 128.2, 120.4, 39.3, 33.9, 21.8 ppm; MS *m/z* 179/178 (M + 1)/M^+ = 3.1:1), 143, 128, 115, 63, 51, 39.

6-Methyl-6-(2-Methyl-1-propenyl)fulvene (8a) (56% isolated yield, NaOMe): ^{1}H NMR (300 MHz, $CDCl_3$/TMS) δ 6.55–6.34 (m, 4 H); 6.2 (s, 1H); 2.28 (s, 3H); 1.90 (d, 0.9 Hz, 3H); 1.79 (d, J = 0.6 Hz, 3H); ^{13}C NMR (75 MHz, CDCl3/TMS) δ 140.2, 131.6, 131.3, 130.8, 127.0, 122.8, 121.2, 121.1, 27.9, 22.1, 21.3 ppm; MS *m/z* 132 (M^+), 117, 91, 39.

6-(2-Methoxy-2-methylpropanyl)-6-methylfulvene (8b) (38% isolated yield, NaOMe): ^{1}H NMR ($CDCl_3$/TMS) δ 6.5 (m, 2H); 6.45 (m, 2H); 3.23 (s, 3H); 2.58 (s, 2H); 2.2 (s, 3H); 1.25 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$, TMS) δ 151.6, 145.6, 131.4, 121.8, 121.44, 76.55, 49.9, 46.88, 26.38, 23.37 ppm; MS *m/z* 178 (M^+), 146, 131.

6-[(*p*-Methoxyphenyl)ethenyl]-6-methylfulvene (9) (71%, NaOH): ^{1}H NMR (300 MHz, $CDCl_3$/TMS) δ 7.51 (d, J = 16.2 Hz, 1H); 7.49 (d, J = 8.5 Hz, 1H); 6.96 (d, J = 16.2 Hz, 1H); 6.92 (d, J = 8.5 Hz, 1H); 6.77 (m, 1H); 6.61 (m, 1H); 6.53 (m, 2H); 3.85 (s, 3H); 2.39 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$/TMS) δ 145.3, 135.2, 132.0, 131.4, 130.3, 129.3, 126.8, 121.7, 119.8, 115.0, 56.0, 17.3 ppm; MS *m/z* 224 (M^+), 208, 193, 123, 165, 115, 91, 89, 40.

6-Methyl-6-(2-phenyl-1-propenyl)fulvene (10) (67%, NaOH): ^{1}H NMR (300 MHz, $CDCl_3$/TMS) δ 7.2–7.6 (m, 5H); 6.74 (s, 1H); 6.52 (m, 2H); 6.42 (m, 2H); 2.37 (s, 3H); 2.18 (s, 3H) ppm; MS 208 (M^+), 193, 165, 115, 91, 89, 51, 39.

6,6-Bis(2-methyl-1-propenyl)fulvene (11) (73%, NaOH): ^{1}H NMR (300 MHz, $CDCl_3$/TMS) δ 6.35–6.5 (m, 4H); 5.96 (m, 2H); 2.09 (s, 6H); 1.80 (s, 6H); ^{13}C NMR ($CDCl_3$/TMS) δ 154.5, 136.5, 131.2, 126.8, 126.0, 121.1, 28.2, 25.7; MS *m/z* 186 (M^+), 123, 55, 39.

2-Phenyl-4-(*p*-tolyl)bicyclo[3.3.0]octa-1,4,6-triene (12): mp 112–115 °C (85%, NaOMe); ^{1}H NMR (300 MHz, $CDCl_3$/TMS) δ 7.1–7.6 (m, 9H); 6.93 (m 1H); 6.65 (m, 1H); 4.1 (s, 2H); 3.395 (br.s, 3.395, 1H); 2.35 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$/TMS) δ 146.8, 143.4, 142.8, 140.1, 137.6, 136.3, 134.2, 132.2, 130.0, 129.3, 128.2, 126.4, 126.3, 48.1, 34.0, 21.9 ppm; MS *m/z* 270 (M^+), 229, 207, 165, 127, 88, 40, 28.

6-Cyclopropylfulvene (13) (74%, pyrrolidine): ^{1}H NMR (300 MHz, $CDCl_3$/TMS) δ 6.55 (m, 1H); 6.45 (m, 1H); 6.10 (m, 1H); 5.7 (d, J = 11 Hz, 1H); 1.98 (m, 1H); 1.0 (m, 2H); 0.65 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$/TMS) δ 149.0, 144.6, 132.9, 130.0, 125.4, 119.7, 15.0, 10.5 ppm; MS *m/z* 118 (M^+), 117, 115, 103, 91, 77, 65, 63, 51, 39.

6-(Chloromethyl)-6-methylfulvene (14) (66%, pyrrolidine): ^{1}H NMR (300 MHz, $CDCl_3$/TMS) δ 6.33–6.6.48 (m, 4H); 4.3 (s, 2H); 2.2 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$/TMS) δ 145.5, 144.1, 134.2, 133.3, 122.1, 120.2, 46.6, 19.6 ppm; MS *m/z* 140/142 (3/1, M^+/(M + 2)), 125, 105, 79, 77, 51, 39.

6-(1-Hydroxyethyl)-6-methylfulvene (15) (85%, pyrrolidine): ^{1}H NMR (300 MHz, $CDCl_3$/TMS) δ 6.45–6.55 (m, 4H); 5.1 (q, J = 6.6 Hz, 1H); 2.2 (s, 3H); 1.36 (d, J = 6.6 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$/TMS) δ 154.0, 142.1, 132.6, 132.1, 122.2, 119.9, 69.4, 22.8, 15.8 ppm; MS *m/z* 136 (M^+), 93, 91, 77, 43.

6-(2-Hydroxyphenyl)fulvene (16) (92%, pyrrolidine): ^{1}H NMR (300 MHz, $CDCl_3$/TMS) δ 7.55 (d, J = 7.5 Hz, 1H); 7.52 (s, 1H); 7.22 (t, J = 7.5 Hz, 1H); 6.95 (t, J = 7.5 Hz, 1H); 6.87 (d, J = 7.5 Hz, 1H); 6.64 (m, 2H); 6.51 (m, 1H); 6.35 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$/TMS) δ 156.0, 145.6, 135.5, 133.9, 132.8, 131.2, 131.1, 127.5, 124.9, 121.0, 116.5 ppm; MS *m/z* 170 (M^+), 169, 141, 115, 39.

6-(2-Hydroxyethyl)-6-methylfulvene (17) (64%, pyrrolidine): ^{1}H NMR (300 MHz, $CDCl_3$/TMS) δ 6.53 (m, 4H); 3.7 (t, J = 6.9 Hz, 2H); 2.84 (t, J = 6.9 Hz, 2H); 2.26 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$/TMS) δ 150.5, 144.3, 132.6, 131.6, 121.2, 121.0, 70.7, 37.6, 22.2 ppm; MS *m/z* 137 (M + 1), 107, 91, 39.

6-(2-Hydroxypropyl)fulvene (18) (41% isolated yield, pyrrolidine): ^{1}H NMR ($CDCl_3$/TMS) δ 6.55 (m, 1H); 6.45 (m, 3H); 6.2 (m, 1H); 4.0 (m, 1H); 2.64 (dd, J = 7.9, 6.16 Hz, 2H); 1.27 (d, J = 6.36, 3H); ^{13}C NMR ($CDCl_3$/TMS) δ 148.0, 137.8, 133.7, 131.3, 125.5, 119.2, 65.8, 40.5, 23.3 ppm; MS *m/z* 136 (M^+), 91, 45.

6-Methyl-6-[1-(methylthio)ethyl]fulvene (19) (81%, pyrrolidine): ^{1}H NMR ($CDCl_3$/TMS) δ 6.56 (m, 2H); 6.48 (m, 2H); 4.2 (q, J = 7.2 Hz, 1H); 2.24 (s, 3H); 1.90 (s, 3H); 1.41 (d, J = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$/TMS) δ 151.6, 143.9, 132.6, 131.5, 122.1, 120.1, 45.4, 19.2, 15.6, 15.3 ppm; MS *m/z* 166 (M^+), 151, 118, 117, 91, 77, 41, 39.

6-Methyl-6-[1-(1,3-oxothiolan-2-yl)ethyl]fulvene (20) (76%, pyrrolidine). Sodium (0.25 g, 10.9 mmol) was added with cooling to 3.8 mL of dry ethanol. To this solution was slowly added a mixture of 0.7 g (10.6 mmol) of cyclopentadiene and 2 g (13.6 mmol) of 2-acetyl-2-methyl-1,3-oxathiolane. The mixture was stirred at room temperature under argon for 1.5

h. The progress of the reaction was monitored by TLC (CH_2Cl_2/petroleum ether, 1/9). After completion of the reaction, 13 mL of H_2O was added, the mixture extracted with ether (3 × 30 mL), the combined ether extracts were washed with water and brine and dried over $MgSO_4$, and the solvent was removed in vacuo. The product was purified using column chromatography on neutral alumina (Brockmann, activity I, CH_2Cl_2/petroleum ether, 1:9). The fulvene was isolated as a bright yellow liquid: ^1H NMR ($CDCl_3$/TMS) δ 6.9 (m, 1 H); 6.45 (m, 3H); 4.3 (m, 1 H); 4.07 (m, 1H); 3.1 (m, 2H); 2.28 (s, 3H); 1.89 (s, 3H) ppm; MS *m/z* 186 (M + 2), 184 (M^+), 103, 61, 43.

Dihydro-*as*-indacenes (22) (55%, pyrrolidine). To a solution of 4 g (0.061 mol) of freshly distilled cyclopentadiene in 10 mL of methanol was added 1.45 g (0.01 mol) of a 40% aqueous solution of glyoxal. The mixture was cooled to 0 °C in an ice–water bath, and 2.89 g (0.041 mol) of pyrrolidine was added dropwise. The mixture was stirred at 0 °C for 2 h under nitrogen. Acetic acid (2.7 g, 0.045 mol) was added then dropwise, and the mixture diluted with ether and water (50 mL each). The aqueous layer was washed with ether (2 × 50 mL), and the combined organic layers were washed with water and brine (25 mL each), dried over $MgSO_4$, and concentrated in vacuo. The crude product was then purified by chromatography on a SiO_2 column, eluting with *n*-hexane, to give 850 mg (55% yield) of a mixture of dihydro-*as*-indacenes. The ^1H NMR spectrum of the mixture **22** was identical in all respects to the one reported by Katz et al.[18b]

3-Hydroxy-3-(1,3-cyclopentadien-1-yl)-2-butanone/3-Hydroxy-3-(1,3-cyclopentadien-2-yl)-2-butanone (23a/24a:1.2/1) (0.18 mmol of 23a/24a, 62%, pyrrolidine). The product was purified by preparative TLC (30% ethyl acetate in petroleum ether): FT-IR (neat, 1.2:1 mixture of **23a/24a**) 3450, 3060, 2981, 1713.3, 1685, 1355.5, 1199, 1128, 1099.5, 1093 cm^{-1}; ^1H NMR ($CDCl_3$/TMS) δ 6.3–6.6 (m, 3H); 4.15 (br s, exchanges with D_2O, 1H); 2.97 (d, ^2J = −23.7 Hz, B part of an AB system, 1H, **23a**); 2.65 (d, ^2J = −23.7 Hz, B part, 1H, **23a**) (2.95) (s, 2H, isomer **24a**); 2.07 (s, 3H); 1.55 (s, 3H); ^{13}C NMR ($CDCl_3$/TMS) δ 210.3 (210.2); 149.6 (148.6); 135.2 (134.14); 132.2 (131.3); 130.2 (129.3), 79.15 (78.4), 42.1 (40.9); 24.6 (24.3), 23.9 (23.7) ppm; MS *m/z* 152 (M^+), 109, 134, 92, 65, 43.

Methyl 2-Hydroxy-2-(1,3-cyclopentadien-1-yl)propanoate/Methyl 2-Hydroxy-2-(1,3-cyclopentadien-2-yl)propanoate (23b/24b:1.5/1) (7.2 mmol of 23b/24b, 69%, pyrrolidine). The product was purified by column chromatography on SiO_2, using 30% ethyl acetate in petroleum ether: FT-IR (neat, mixture **23b/24b**) 3450, 3060, 3000, 2970, 1736, 1640, 1448, 1432, 1368, 1352, 1256, 1144, 976, 896, 680 cm^{-1}; ^1H NMR ($CDCl_3$/TMS) δ 6.3–6.7 (m, 3H); 3.8 (3.78) (s, 3H); 3.2 (br s, 1H); 3.06 (d, ^2J = −12 Hz, B part of an AB system, 1H, **23b**) (3.0, s, 2H, isomer **24b**); 2.98 (d, ^2J = −12 Hz, B part, 1H, **23b**); 1.65 (s, 3H) ppm; MS *m/z* 168 (M^+), 150, 109, 65, 43.

6-Methyl-6-[1-(ethenyloxy)ethyl]fulvene (26). A mixture of 10 g (0.074 mol) of fulvene **15**, 54 g (0.75 mol, 71.62 mL) of ethyl vinyl ether, and 0.82 g (2.6 mmol) of mercuric acetate was refluxed under nitrogen for 5 h with stirring. The mixture was then cooled to room temperature and treated with 3 g of solid potassium carbonate. The filtered mixture was then dissolved in diethyl ether, washed with water (50 mL), and dried over potassium carbonate. The solvent was removed in vacuo and the product isolated by column chromatography on SiO_2 (petroleum ether) (8.15 g, 0.05 mol, 68%): ^1H NMR ($CDCl_3$/TMS) δ 6.5 (m, 4H); 6.3 (dd, J = 14.1, 6.6 Hz, 1H); 5.13 (q, J = 6.6 Hz, 1H); 4.25 (dd, J = 14.1, 1.8 Hz, 1H); 3.98 (dd, J = 6.6, 1.8 Hz, 1H); 2.13 (s, 3H); 1.44 (d, J = 6.6 Hz, 3H); ^{13}C NMR ($CDCl_3$/TMS) δ 151.9, 150.7, 143.2, 132.7, 132.6, 122.1, 119.5, 89.9, 76.4, 21.5, 15.0; MS *m/z* 162 (M^+), 144, 129, 128, 105, 91, 40.

6-Methyl-6-[1-(methylsulfinyl)ethyl]fulvene (27). A 0.5 M solution of sodium metaperiodate ($NaIO_4$, 3.5 mmol, 7.0 mL) at 0 °C was added to a 10 mL methanol solution of fulvene **19** (0.44 g, 2.9 mmol). The mixture was stirred in an ice bath for 4 h while the progress of reaction was monitored by TLC (15% ethyl acetate in petroleum ether). The precipitate (sodium iodate) was removed by vacuum filtration, and the filtrate was extracted with CH_2Cl_2 (2 × 50 mL). The combined extracts were dried over anhydrous $MgSO_4$, and the solvent was removed in vacuo. The crude product was >95% pure (yield: 0.38 g, 2.3 mmol, 78% yield). A sample was purified by preparative TLC for characterization purposes (15% ethyl acetate/petroleum ether): FT-IR (neat) 3073, 2997, 2941, 1632, 1418.4, 1449, 1378, 1306.4, 1224.9, 1041.6, 944.8, 765, 665 cm^{-1}; ^1H NMR ($CDCl_3$/TMS) δ 6.55 (m, 2H); 6.48 (m, 2H); 4.04 (q, J = 7.2 Hz, 1H); 2.5 (s, 3H); 2.19 (s, 3H); 1.67 (d, J = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$/TMS) δ 146.5, 144.7, 133.6, 133.45, 121.4, 119.96, 60.5, 38.2, 17.95, 14.0; MS *m/z* 182 (M^+); 152, 105, 77, 51.

6-Methyl-6-[(phenylsulfinyl)methyl]fulvene (28). The oxidation with $NaIO_4$ was performed under the same conditions as for **14** (2.5 mmol of **29** was used) (207 mg, 0.9 mmol, 36%): FT-IR (neat) 3073.4, 2988, 2923, 1643, 1482.4, 1452.3, 1367, 1101, 1066, 1035.7, 769.7, 744.6, 699.4 cm^{-1}; ^1H NMR ($CDCl_3$/TMS) δ 7.4–6 (m, 5H); 6.3–5 (m, 3H); 6.03 (m, 1H); 4.06 (d, ^2J = 12 Hz, A part of an AB system, 1H); 3.82 (d, ^2J = 12 Hz, B part, 1H); 2.14 (s, 3H); ^{13}C NMR ($CDCl_3$/TMS) δ 148.2, 143.9, 138.3, 133.5, 133.0, 132.1, 129.8, 124.8, 121.1, 120.9, 66.1, 22.9 ppm; MS *m/z* 231 (M + 1), 197, 165, 121, 109, 77, 40.

6-Methyl-6-[(phenylthio)methyl]fulvene (29). To a magnetically stirred solution of 0.14 g (3.6 mmol) of NaOH in 5 mL of methanol, kept under nitrogen and cooled in an ice–water bath, was added 0.39 g (3.6 mmol) of thiophenol. After 5 min was added 0.5 g (3.6 mmol) of **14**. The reaction mixture was stirred for 30 min, diluted with 50 mL of water, and extracted with ether (2 × 30 mL). The combined ether extracts were washed with water, 10% aqueous NaOH, and brine and dried over $MgSO_4$, and the solvent was removed in vacuo (690 mg, 3 mmol, 83%): FT-IR (neat) 3080, 3051, 2965, 2919, 2867, 1641, 1583, 1477, 1439, 1364., 1100 1071, 1025, 771, 739, 689 cm^{-1}; ^1H NMR ($CDCl_3$/TMS) δ 7.1–7.4 (m, 5H); 6.35 (m, 2H); 6.2 (m, 1H); 6.03 (m, 1H); 3.9 (s, 2H); 2.2 (s, 3H); ^{13}C NMR (C_3D_6O/TMS) δ 146.5, 145.4, 136.4, 132.6, 131.9, 131.8, 129.7, 127.7, 121.8, 121.1, 40.7, 20.2 ppm; MS *m/z* 215 (M + 1), 214 (M^+), 165, 105, 40.

1-Methylspiro[2.4]hepta-4,6-diene-1-carbonitrile (30). To a stirred solution of 0.131 g (2.67 mmol) of NaCN in 4 mL of dry DMSO was added 0.30 g (2.13 mmol) of **14** under a nitrogen atmosphere. The mixture was stirred for 10 min, diluted with 50 mL of water, and extracted with ether (2 × 15 mL), the combined ether extracts were washed with water and brine and dried over $MgSO_4$, and the solvent was removed in vacuo. The crude product was more than 90% pure (by NMR). It was purified by TLC on SiO_2 (5% ethyl acetate in petroleum ether) (200 mg, 1.53 mmol, 72%): FT-IR (neat) 3066, 2965, 2915, 2244, 1639, 1450, 1377, 1143, 1093, 1078, 961, 913 cm^{-1}; ^1H NMR ($CDCl_3$, TMS) δ 6.6 (m, 1H); 6.54 (m, 1H); 6.3 (m, 1H); 6.06 (m, 1H); 2.2 (d, ^2J = 5.0 Hz, A part of an AB system, 1H); 1.86 (d, ^2J = 5.0 Hz, B part, 1H); 1.64 (s, 3H); ^{13}C NMR ($CDCl_3$, TMS) 137.7, 134.6, 133.3, 132.3, 123.04, 46.85, 25.1, 20.96, 19.01 ppm; MS *m/z* 132 (M + 1), 93, 66, 39.

6-Methyl-6-(thiocyanatomethyl)fulvene (31). To a magnetically stirred solution of 0.25 g (2.6 mmol) of KSCN in 5 mL of dimethyl sulfoxide was added, under nitrogen, 0.30 g (2.1 mmol) of **14**. The mixture was stirred at room temperature for 2.5 h, diluted with 20 mL of water, and extracted with ether (2 × 30 mL). The ether extracts were combined, washed with water and brine, and dried over $MgSO_4$, and the solvent was rotoevaporated (256 mg, 1.6 mmol, 75%): FT-IR (CCl_4) 3078, 2922, 2853, 2163, 1642, 1556, 1478, 1439, 1366, 1262, 1229, 1098, 995 cm^{-1}; ^1H NMR ($CDCl_3$/TMS) δ 6.55 (m, 3H); 6.47 (m, 1H); 6.4 (m, 1H); 3.99 (s, 2H); 2.32 (s, 3H); ^{13}C NMR ($CDCl_3$/TMS) δ 147.41, 140.42, 134.82, 134.02, 121.9, 120.31, 111.89, 39.58, 20.26 ppm; MS *m/z* 163 (M^+), 148, 130, 105, 79, 77, 40.

1,1-Dimethylspiro[2.4]hepta-4,6-diene (32). To a stirred solution of 0.3 g (2.1 mmol) of **14** in 4 mL of dry ether was added dropwise 1.65 mL of a 1.4 M ethereal CH_3Li (2.13 mmol) solution at 0 °C. The ice bath was removed and the mixture stirred at room temperature for 20 min. Then it was poured onto 10 g of ice–water, the layers were separated, the ethereal layer was washed with brine and dried over $MgSO_4$, and the

solvent was removed in vacuo. The residue was purified by column chromatography on SiO_2 using pentane as eluent (252 mg, 1.3 mmol, 62%). This compound was identical in all respects to a sample prepared by an alternative method.[20]

6-(2-Hydroxy-2-phenylethyl)-6-methylfulvene (33). To 0.09 g (3.7 mmol) of magnesium turnings in 5 mL of dry ether was slowly added 0.5 g (3.6 mmol) of **14** in 5 mL of dry ether, while stirring under a nitrogen atmosphere. The mixture was stirred at room temperature for 15 min, and then 0.36 g (3.4 mmol) of benzaldehyde in 3 mL of ether was added dropwise at 0 °C. After the addition was complete, the ice bath was removed, and the mixture stirred at room temperature for 35 min and then poured onto 25 mL of cold aqueous NH_4Cl. More ether (30 mL) was added to the solution, the layers were separated, the aqueous was extracted twice with 10 mL portions of ether, and the combined ether extracts were washed with water and then brine. After drying over $MgSO_4$ the solution was rotoevaporated and the residue purified by preparative TLC on SiO_2 (30% ethyl acetate in petroleum ether) (404 mg, 1.9 mmol, 56%). The spectral data of **33** were identical to those reported in literature.[21]

6-(Azidomethyl)-6-methylfulvene (34). To a magnetically stirred solution of 0.67 g (10 mmol) of NaN_3 and 0.42 g (7 mmol) of urea in 40 mL of dry DMF was added under nitrogen 1.2 g (8.5 mmol) of **14**. The mixture was stirred for 30 min, diluted with 100 mL of water, and extracted with ether (2 × 30 mL). The combined ether extracts were washed with water, saturated $NaHCO_3$ and with brine, and dried over $MgSO_4$, and the solvent was removed by rotoevaporation. The product was more than 95% pure by NMR and needed no further purification (835 mg, 5.6 mmol, 66%): FT-IR (neat) 3073, 2974, 2940, 2849, 2108, 1655, 1483, 1367, 1340, 1280, 1250, 1203, 1099, 780, 630 cm^{-1}; ^1H NMR ($CDCl_3$, TMS) δ 6.54 (m 3H); 6.44 (m 1H); 4.17 (s, 2H); 2.26 (s, 3H); ^{13}C NMR ($CDCl_3$/TMS) δ 146.1, 143.3, 133.98, 133.27, 121.9, 120.4, 55.3, 20.1 ppm; MS m/z 119 (M − N_2), 104 (M − HN_3), 91, 77, 44, 41.

Acknowledgment. This work was supported by the National Science Foundation under Grant No. CHE-8904016. We thank Dr. Scott Gronert, San Francisco State University, for helpful discussions, and Ms. Greta Gabrielle Glugoski, Mr. Jim Li, Matthew Ludeman, Vinh P. T. Nguyen, and Cynthia Wong for technical assistance. Ms. Madeleine Ossun is a recipient of a 1994 Department of Education Scholarship for Women and Minorities.

Supplementary Material Available: ^1H NMR and/or ^{13}C NMR spectra for all new compounds, **1**−**9**, **11**−**20**, **23**, **24**, **26**−**31**, and **34** (45 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

JO941580J