Tetrahedron Vol. 50, No. 1, pp. 61-76, 1994
Printed in Great Britain

0040-4020/94 $6.00+.00

Regioselective Palladium-Catalyzed Allylation of Fulvenes[1]

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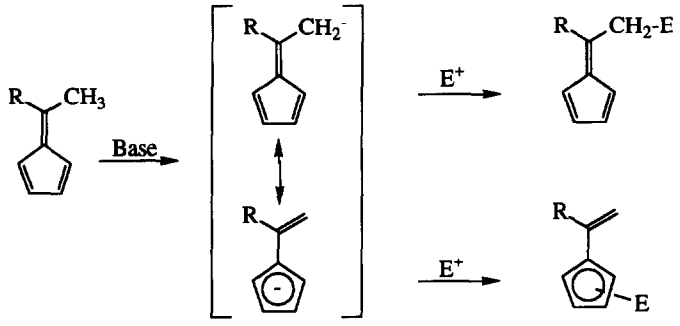
Abstract: Fulvene-anions (vinyl cyclopentadienyl anions) are exclusively allylated in the exocyclic position by allylic chlorides, allylic acetates, and allylic carbonates in the presence of catalytic amounts of bis(dibenzylideneacetone)palladium(0) and triphenyl phosphine in good to excellent yield. A high degree of regioselectivity is observed with regard to the allylic substrate, and the most hindered position was predominately substituted. Inversion of stereochemistry of the allylic carbon by migration of the anion from the metal, of an intermediate η^3-allylpalladium complex, to carbon is observed.

INTRODUCTION

Numerous papers and reviews[4] have been published on 5-alkylidene-1,3-cyclopentadienes since the first preparation thereof by Thiele in 1900.[5] This class of compounds, more commonly called fulvenes,[6] have received considerable interest, both from theoretical and synthetic chemists. Although fulvenes are commonly used as ligands as such or as precursors to cyclopentadienyl ligands in organometallic chemistry,[7] we are interested in fulvenes as potentially useful precursors in natural product synthesis. To date, a number of syntheses have been published utilizing fulvenes as key intermediates including the synthesis of hirsutene,[8] capnellene,[9,10] β-vetivone,[11] viburtinal,[12] hinesol,[13] silphinene,[14] and longifolene.[15]

The most widely used fulvene synthesis is that of Thiele which consists of condensation of 1,3-cyclopentadiene with aldehydes or ketones in the presence of a base, using an alcohol as solvent.[16] Although good yields of fulvenes are usually obtained by this method, for the synthesis of more elaborate natural products or new organometallic ligands, the required aldehydes or ketones may not be readily available. Thus, it would be of importance to develop a method to further regioselectively modify fulvenes, prepared by the standard Knoevenagel-type condensation.

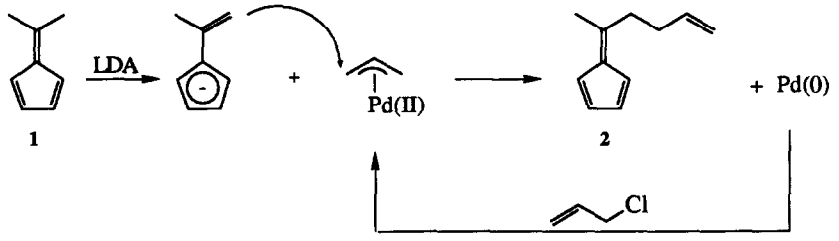
An attractive protocol for the functionalization of fulvenes would be deprotonation to a fulvene-anion followed by reaction with an electrophile. The fulvene-anions are ambident electrophiles, however, and only addition to the 7-position would yield a fulvene-product. The regiochemical outcome depends on the nature of the electrophile, and softer electrophiles such as aldehydes add preferentially to the exocyclic 7-position of the anion whereas harder electrophiles such as protons and alkyl- and allyl-halides add to a ring position (Scheme 1).[17] In the case of allylic chlorides (and allylic acetates), we recently found that the anion of 6,6-dimethylfulvene could be allylated at the exocyclic 7-position in the presence of a palladium-phosphine catalyst.[18] Herein is a full account of a more general study of this reaction, undertaken in our laboratories. The regio- and stereochemical outcome of the reaction will be discussed.



Scheme 1

RESULTS AND DISCUSSION

The acidity of fulvenes is comparable to ketones, and fulvene anions are smoothly formed by deprotonation with lithium diisopropylamide in tetrahydrofuran.[19] The deprotonation is conveniently monitored visually by the disappearance of the fulvene color (yellow for unconjugated fulvenes)[20] to the colorless fulvene anions. The anions were allowed to react with allylic electrophiles in the presence of a palladium(0) catalyst. Typically, the anion of 6,6-dimethylfulvene (**1**)[21] was added dropwise to a -30 °C cold solution of 3-chloro-1-propene in the presence of 4 mol % bis(dibenzylideneacetone)palladium(0) and 10 mol % triphenyl phosphine in tetrahydrofuran. The reaction mixture was stirred for 40 min., quenched with aqueous ammonium chloride followed by workup giving 6-methyl-6-(3-butenyl) fulvene **2** in 82% isolated yield (Scheme 2).



Scheme 2

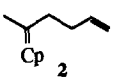
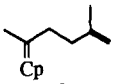
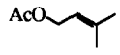
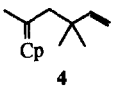
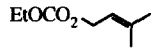
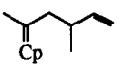
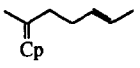
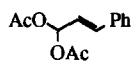
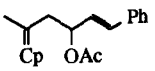
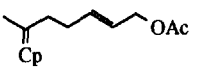
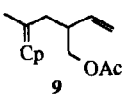
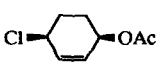
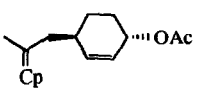
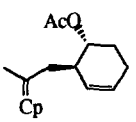
It should be noted that, upon reaction of the anion of **1** with 3-chloro-1-propene in the absence of catalyst, a complex mixture of ring allylated products was isolated. A plausible mechanism for the catalyzed reaction involves the formation of an intermediate η^3-allylpalladium complex from the reaction of the chloride with the palladium catalyst. Nucleophilic substitution of this complex by the exocyclic position of the anion of **1** forms the isolated product and regenerates the palladium(0) catalyst (Scheme 2).

A number of other allylic chlorides, acetates, and carbonates gave similar allylation products when reacted with the anion of **1** employing the same protocol. The results thereof are summarized in Table 1. Based on NMR analysis of the crude reaction mixture, cyclopentadienyl adducts were not observed, indicating a complete selectivity for exocyclic allylation of the dimethylfulvene anion. A slight excess of the fulvene anion gave in many cases useful yields since bisallylation was not a serious side-reaction. One exception is allyl chloride where 25-39% of bisallylation was obtained when 1 equivalent of electrophile was used. The fulvene products suffer from partial dimerization and/or polymerization which account in some cases for the moderate yield obtained after purification. The η^3-allylpalladium intermediates formed from these substrates are preferentially substituted at the more hindered termini of the allylic moiety. For example, 1-acetoxy-3-methyl-2-butene was exclusively substituted in the tertiary position (entry 3) and 1-chloro-2-butene gave an 11:2 mixture in favor of the more hindered product (entry 6).

In a comparison study, a substantially lower yield of product was obtained when ethyl 3-methyl-2-butenyl carbonate was used in place of 1-acetoxy-3-methyl-2-butene (entries 3 and 4). Furthermore, the yield of **4** employing the carbonate dropped from 41% to 26% when the reaction time was extended from 100 min. to 460 min. (entry 5). A possible explanation for the decrease in yield is that lithium ethoxide, formed in the reaction between the carbonate and palladium(0), further reacts with the fulvene product causing isomerization and polymerization thereof. In a separate experiment, 6,6-dimethylfulvene was recovered unchanged upon reaction with ethyl 3-methyl-2-butenyl carbonate, bis(dibenzylideneacetone)palladium(0), and triphenylphosphine. 1,1-Diacetoxy-3-phenyl-2-propene cleanly afforded the adduct **7** (entry 7). This regioselectivity has also been observed upon reaction of 1,1-diacetoxy-3-phenyl-2-propene with dimethyl malonate in the presence of a palladium(0) catalyst.[22]

The well precedented palladium-catalyzed reaction of 1,4-chloro-acetates, such as *trans*-4-acetoxy-1-chloro-2-butene or *cis*-1-acetoxy-4-chloro-2-cyclohexene, with stabilized nucleophiles such as malonates, usually affords allylated products with a high degree of regioselectivity in favor of the 1,4-adduct.[23] Furthermore, the process leads to overall retention of stereochemistry at the allylic position since oxidative addition to form the intermediate η^3-allylpalladium complex and subsequent nucleophilic attack on the η^3-allyl ligand both occur with inversion of configuration. Somewhat to our surprise, both 1,2- and 1,4-addition products were isolated upon reaction of these electrophiles with **1** (entries 8-10). Furthermore, the regiochemistry of the allylation using chloro-acetates was found to be highly temperature dependent. Thus, *trans*-4-acetoxy-1-chloro-2-butene gave a 3:1 ratio of 1,4-/ 1,2-adduct upon reaction with **1** at 25 °C. In contrast, performing the reaction at 0 °C gave a 2:5 ratio in favor of the 1,2-adduct. We do not presently have an explanation for this change in selectivity. The regiochemical outcome suggests a migration of the nucleophile from metal to the allylic substrate of an intermediate η^3-allyl complex, and the stereochemistry was tentatively assigned as seen in Table 1.[24]

Table 1. Palladium-Catalyzed Allylation of 6,6-Dimethylfulvene (1).

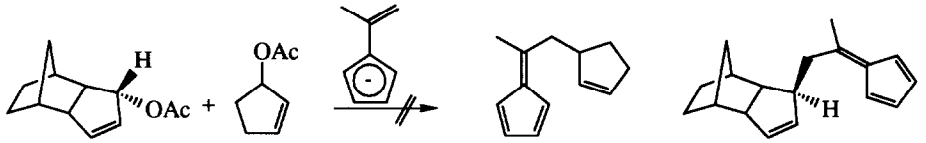
Entry	Electrophile	Conditions[a]	Product(s)[b]	% Yield[c]
1		-30 °C, 40 min	 **2**	82
2		0 °C, 25 min	 **3**	61
3		25 °C, 5 h	 **4**	68
4		25 °C, 100 min	**4**	41
5		25 °C, 460 min	**4**	26
6		25 °C, 90 min	 **5**  **6**	40 (11:2)
7		25 °C, 2 h	 **7**	48
8		25 °C, 1 h	 **8**	46 (3:1)
9		0 °C, 22 min	 **9**	70 (2:5)
10		0 °C, 30 min	 **10**  **11**	83

a) For details, see the Experimental Section. b) Cp = cyclopentadienylidene. c) Yield refers to pure isolated compounds.

The regiochemistry of the products **8-11** was assigned by ^{1}H NMR spectroscopy, based on the significant downfield shift (ca 0.6 ppm) seen for allylic CH-OAc protons versus their saturated counterparts. In our case, the proton geminal to the acetoxy group in **8** and **10** resonates at δ 5.30 and 4.60 ppm respectively, compared to those of **9** and **11** resonating at δ 4.75 and 4.03.

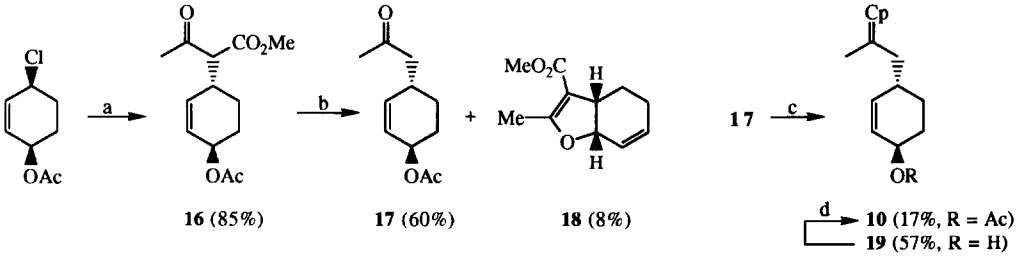
An initial attempt to resolve the question whether a trans or cis attack of the nucleophile on the intermediate η^3-allylpalladium complex had occurred, was made by employing the protocol developed by Fiaud and Legross.[25] Thus, upon reaction of a 1:1 mixture of the allylic acetate **12** and 3-acetoxy-1-cyclopentene (**13**)

with the anion of **1**, a small amount of what appeared to be allylation product of the latter was isolated together with a large amount of polymeric material (Scheme 3). In addition, the product **15** was not detected, and the allylic acetate **12** was recovered in almost quantitative yield.



Scheme 3

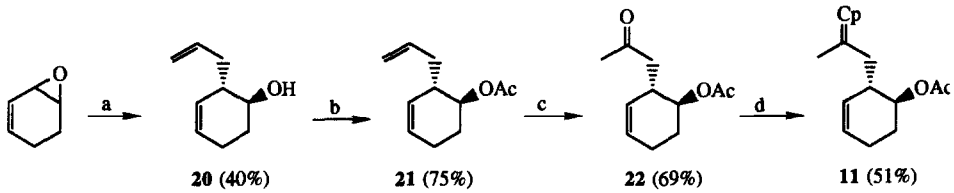
This result was seen as an indication of a trans-attack affording a product with retention of stereochemistry of the allylic substrate. However, control experiments showed that neither 3-acetoxycyclopentene (**13**), nor 3-chlorocyclopentene gave the fulvene allylation product **14** upon reaction with the anion of 6,6-dimethyl-fulvene (**1**). The starting materials were consumed in both these reactions, and complex mixtures of unidentified hydrocarbons were isolated. For reasons not understood, no allylation of **1** occurred by either **12** or **13** despite several attempts. In light of the inconclusive results presented above, it was found necessary to secure the stereochemistry of the products **10** and **11** by independent syntheses. Moreover, corroboration of the stereochemistry would provide an insight into the reaction mechanism. The fulvene **10** was prepared by reaction of *cis*-1-acetoxy-4-chloro-2-cyclohexene with sodium methyl acetoacetate, a reaction known to proceed with inversion of stereochemistry (Scheme 4).[26] The expected *trans*-1,4-addition adduct **16** was isolated in 85% yield after chromatography. Decarboxylation of **16**, employing lithium chloride in aqueous dimethyl sulfoxide at 175 °C,[27] gave the ketone **17** in 60% yield together with the tetrahydrobenzofuran **18** (8%). The acetoacetate adduct **16** readily undergoes enolization-ring closure at elevated temperatures to form the benzofuran **18.** Condensation of **17** with 1,3-cyclopentadiene gave the fulvene **10** in 17% yield together with the fulvene alcohol **19** in 57%. Treatment of the alcohol **19** with 4-(*N,N*-dimethylamino)pyridine and acetic anhydride in diethyl ether gave a 36% yield of **10**. The low yield was apparently due to rapid polymerization of the starting material as evident by the large amount of insoluble yellow residue remaining in the reaction flask.



a) Sodium methyl acetoacetate, MeCN, Δ_x; b) LiCl, H_2O, DMSO, Δ; c) Pyrrolidine, 1,3-cyclopentadiene, MeOH; d) Ac_2O, DMAP, Et_2O, 36%.

Scheme 4

The synthesis of **11** was achieved in a four step sequence. Reaction of 1,3-cyclohexadiene monoepoxide with allylmagnesium chloride gave *trans*-alcohol **20** (Scheme 5).[28] The alcohol was acetylated with acetic anhydride in the presence of DMAP to afford **21**. Wacker oxidation[29] of **21** followed by condensation of the obtained ketone **22** with 1,3-cyclopentadiene, produced the fulvene **11** in 51% yield. The *trans*-fusion of **21** and **22** was confirmed by the coupling constants between **CH**-OAc and **CH**-$CH_2CH{=}CH_2$ and **CH**-OAc and **CH**-CH_2COCH_3 being 10.4 and 11.2 Hz respectively.[30] Prolonged reaction times only resulted in a lower yield of **11** and since no adduct derived from cleavage of the ester was seen this observation is probably due to polymerization of **11**. The spectral data (NMR and GC-MS) for **10** and **11**, prepared as described above (Schemes 4 and 5), were in all respects identical to those recorded from the products obtained by the palladium-catalyzed reaction of *trans*-1-acetoxy-4-chloro-2-cyclohexene and the anion of 6,6-dimethylfulvene, thus securing the assigned stereochemistry.



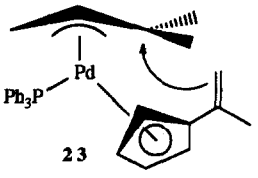
20 (40%) **21** (75%) **22** (69%) **11** (51%)

a) $CH_2{=}CH\text{-}CH_2MgCl$; b) Ac_2O, DMAP, pyridine; c) $PdCl_2$, CuCl, H_2O/DMF, O_2; d) Pyrrolidine, 1,3-cyclopentadiene.

Scheme 5

According to Fiaud and Legros, the cyclopentadienyl anion prefers to react with to a η^3-allylpalladium complex trans to the metal, whereas the indenyl anion was found to react via a prior coordination to palladium, followed by migration.[25] Fulvene anions (*cf.* vinylcyclopentadienyl) anions thus fall in the category of nucleophiles that will be allylated by a η^3-allylpalladium phosphine complex via *cis*-migration from the metal. Since cyclopentadienyl anions are good ligands for Pd(II), it is conceivable that allylation of fulvene anions with η^3-allylpalladium complexes proceeds via an intermediate complex **23** (Figure 1).

Figure 1



23

A selection of 6-substituted fulvenes, prepared by condensation of 1,3-cyclopentadiene with aldehydes or ketones, was reacted with 3-chloro-1-propene forming allylated products in good yield (Table 2). All fulvenes showed complete selectivity for allylation of the intermediate fulvene anion at the exocyclic 7-position. Reaction of 6-methyl-6-(1-methylethyl)fulvene **24** gave exclusively allylation in the least hindered position affording the fulvene **25** (entry 1) suggesting a regioselective deprotonation in favor of the least hindered acidic position in

24. No product derived from addition of the allyl group to the more substituted isopropyl substituent was observed (GLC). Both secondary and tertiary fulvene anions can be allylated employing the described procedure as exemplified in entries 2, 4, and 5 in Table 2. However, reaction of the tertiary anion formed from **32** gave a poor yield of product.

Table 2. Palladium-Catalyzed Allylation of 6-Substituted Fulvenes.

Entry	Fulvene[a]	R	R'	R''	Product (% Yield)[b]
1	**24**	Me_2CH	H	H	**25** (69)
2	**26**	$CH_2CH_2CH_2CH_2$		H	**27** (48)
3	**28**	Ph	H	H	**29** (69)
4	**30**	H	Me	H	**31** (62)
5	**32**	H	Me	Me	**33** (23)

a) The fulvene anion was added to a - 30 °C THF solution of 3-chloro-1-propene (1.5 equiv.), $Pd(dba)_2$, and PPh_3 whereafter the reaction mixture was stirred at ambient temperature for 1.5 h. b) Yield refers to pure isolated compounds.

In summary, a novel method to functionalize 6-substituted fulvenes at the exocyclic position employing allylic electrophiles in the presence of a palladium(0) catalyst has been developed. A high degree of regioselectivity with regard to the allylic substrate was observed, and the most substituted position was allylated. In addition, inversion of stereochemistry of the allylic position was seen.

EXPERIMENTAL SECTION

General Procedures. All NMR spectra were determined in $CDCl_3$ and the chemical shifts are expressed in δ values relative to Me_4Si (0.00 ppm, ^1H and ^{13}C), $CHCl_3$ (7.26 ppm ^1H), or $CDCl_3$ (77.00 ppm, ^{13}C) internal standards. ^1H-^1H coupling constants are reported as calculated from spectra; thus a slight difference between $J_{a,b}$ and $J_{b,a}$ is usually obtained.

The following chemicals were prepared according to literature procedures: Bis(benzylideneacetone)-palladium(0),[31] 3-methyl-1-acetoxy-2-butene,[32] *trans* -4-acetoxy-1-chloro-2-butene,[33] *cis* -1-acetoxy-4-chloro-2-cyclohexene,[33] 1,1-diacetoxy-3-phenyl-2-propene,[34] 1-acetoxy-3a,4,5,6,7,7a-hexahydro-(3β,3aα,4α,7α,7aα)–4,7–methano-1H -indene (**12**),[25] 3-acetoxy-2-pentene,[35] 1,3-cyclohexadiene

monoepoxide,[36] 6, 6-dimethylfulvene (**1**),[17] 6-methyl-6-(1-methylethyl)fulvene (**26**),[17] 6,6-tetramethylene-fulvene (**28**),[17] 6-methyl-6-phenylfulvene (**30**),[37] 6-ethylfulvene (**32**),[38] 6-(1-methylethyl)fulvene (**34**).[17]

All other chemicals used herein were obtained from commercial sources and used as received. Tetrahydrofuran (THF) and diethyl ether were distilled from sodium benzophenone ketyl prior to use. All reactions were performed under a nitrogen atmosphere in oven dried glassware. Correct elemental analysis for the prepared fulvenes could not be obtained due to their low thermal stability. Polymerization was observed upon standing overnight at room temperature or after a few weeks at -20 °C.

6-(3-Butenyl)-6-methylfulvene(2). To a -78 °C cold solution of 1.21 g (12.0 mmol) of diisopropyl-amine in 30 mL of THF was added, by syringe, 6.87 mL (11.0 mmol, 1.6 M in hexanes) of n-butyllithium. The clear solution was removed from the cold-bath and stirred at ambient temperature for 5 min. The solution was recooled to -78 °C and 1.06 g (10.00 mmol) of 6, 6-dimethylfulvene (**1**) was added dropwise by syringe. The resulting pale peach-colored solution was stirred at ambient temperature for 5 min. to ensure complete formation of the anion, then recooled to -78 °C. To a -30 °C solution of 230 mg, (0.4 mmol) of $Pd(dba)_2$ and 262 mg (1.0 mmol) of PPh_3 in THF (30 mL) was added, by syringe, 1.12 g (15.0 mmol) of 3-chloro-1-propene, followed by dropwise addition of **1** via a canula. Upon addition of the anion, the color changed to green-yellow. The reaction mixture was stirred at -30 °C for 40 min., whereafter aqueous NH_4Cl (sat., 20 mL) was added. After stirring for 15 min., the resulting mixture was extracted with diethyl ether (2 x 50 mL); the combined organic phase was washed with aqueous NH_4Cl (sat., 2x10 mL), brine (20 mL), and dried ($MgSO_4$). The solvent was removed on a rotary evaporator at water aspirator pressure, followed by short-path distillation of the residue, to afford 1.20 g (8.2 mmol, 82%) of **2** as a yellow oil. Spectral data (^1H, ^{13}C, MS) for **2** were in complete accordance with literature values.[39]

The following compounds were prepared according to the above procedure employing lithium diisopropylamide (LDA) to form the anions. Either n-butyllithium or t-butyllithium were used, with similar result, to prepare LDA. Commercially available (Aldrich Chem. Co.) LDA, as a THF complex, in cyclohexane also gave satisfactory yields of products. The fulvene anion was always added to a - 30 °C cold THF solution of the electrophile, $Pd(dba)_2$ and PPh_3, whereafter the reaction mixture was stirred at the temperature indicated. The products were purified either by short-path distillation or by flash chromatography of the crude reaction mixture obtained after extraction and solvent removal.

6-Methyl-6-(3-methyl-3-butenyl)fulvene(3). Reaction as above of 98 μL (1.00 mmol) of 3-chloro-2-methyl-propene with 1.08 mmol of the anion of **1** in the presence of 9.2 mg (0.016 mmol) of $Pd(dba)_2$ and 8.7 mg (0.033 mmol) of PPh_3 in 7 mL of THF for 25 min. at 0 °C, gave after distillation, 98 mg (0.61 mmol, 61%) of **3** as a yellow oil. ^1H NMR (90 MHz) δ 6.48 (s, 4H), 4.74 (s, 2H), 2.69 (m, 2H), 2.20 (s, 3H), superimposed on 2.2 (m, 2H), 1.76 (s, 3H); ^{13}C NMR (22.5 MHz) δ 153.2 (s), 144.9 (s), 142.7 (s), 130.8 (d), 130.7 (d), 120.7 (d) 120.2 (d) 110.6 (t), 37.4 (t), 35.4 (t), 22.4 (q), 20.8 (q); IR (film) 3070, 2980, 2960, 2925, 1630, 1440, 1360, 1085, 885, 760 cm^{-1}; GLC-MS (EI) *m/z* 160 (M^+); HRMS (EI) exact mass calcd for $C_{12}H_{16}$ *m/z* 160.1252, obsd 160.1263.

6-(2,2-Dimethyl-3-butenyl)-6-methylfulvene(4). Reaction of 115 mg (1.03 mmol) of 3-methyl-1-acetoxy-2-butene with 1.19 mmol of the anion of **1** in the presence of 9.2 mg (0.016 mmol) of $Pd(dba)_2$ and 8.7 mg (0.033 mmol) of PPh_3 in 7 mL THF for 3 h at ambient temperature, gave after chromatography (hexanes), 121 mg (0.70 mmol, 68%) of **4** as a yellow oil. ^1H NMR (90 MHz) δ 6.49 (m, 4H), 5.92 (dd, 1H, J=17.6, 10.2 Hz), 5.00 (m, 1H), 4.88 (m, 1H), 2.57 (br s, 1H), 2.20 (s, 3H), 2.15 (br s, 1H), 1.07 (s, 6H); ^{13}C NMR (22.5 MHz) δ 151.0 (s), 148.4 (s), 130.7 (d), 130.3 (d), 121.5 (d), 120.6 (d), 113.2 (d), 110.5 (t), 49.5 (t), 38.2 (s), 27.7 (q, 2C), 26.9 (q); IR (film) 3070, 2960, 2920, 2860, 1625, 1460, 1360, 1170, 1080, 990, 910, 760, 615 cm^{-1}; GLC-MS (EI) *m/z* 174 (M^+); HRMS (EI) exact mass calcd for $C_{13}H_{18}$ *m/z* 174.1409, obsd 174.1409.

A similar reaction of 790 mg (5.00 mmol) of ethyl 3-methyl-2-butenyl carbonate in place of 3-methyl-1-acetoxy-2-butene with 5.30 mmol of the anion of **1** in the presence of 121 mg (0.21 mmol) of $Pd(dba)_2$ and 110 mg (0.42 mmol) of PPh_3 in 28 mL THF for 100 min. at ambient temperature, gave after chromatography (hexanes), 357 mg (2.05 mmol, 41%) of **4** as a yellow oil. Longer reaction times gave lower yields of product.

6-(2-Methyl-3-butenyl)-6-methylfulvene(5) and 6-(3-Pentenyl)-6-methylfulvene(6). Reaction of 1.36 g (15.0 mmol) of 1-chloro-2-butene with 10.0 mmol of the anion of **1** in the presence of 230 mg (0.40 mmol) of $Pd(dba)_2$ and 210 mg (0.80 mmol) of PPh_3 in 20 mL THF for 1.5 h at ambient temperature, gave after chromatography (pentane), 634 mg (0.70 mmol, 40%) of an inseparable 11:2 mixture of **5** and **6** as a yellow oil. Spectral data from an 11:2 mixture of **5** and **6**:
^1H NMR (90 MHz) δ 6.47 (s, 8H), 5.65-5.30 (m, 3H), 4.98 (m, 1H), 2.67-2.19 (m, 7H), 2.19 (s, 4H), 1.60 (d, J = 5.2 Hz, 3H); ^{13}C NMR (22.5 MHz) δ 151.4, 143.3, 142.8, 130.8 (d), 130.5 (d), 129.0 (d), 124.7 (d), 120.6 (d), 120.3 (d), 112.8 (t), 43.7 (t), 36.9, 36.6, 26.5 21.0, 20.8, 19.8, 12.6 (q); IR (film) 3100, 3070, 3010, 2920, 2850, 1630, 1440, 1360, 1080, 905, 760, 730 cm^{-1}; GLC-MS (EI, **5**) *m/z* 160 (M^+); GLC-MS (EI, **6**) m/z 160 (M^+); GLC-HRMS (EI, **5**) exact mass calcd for $C_{12}H_{16}$ *m/z* 160.1252, obsd 160.1250; GLC-HRMS (EI, **6**) exact mass calcd for $C_{12}H_{16}$ *m/z* 160.1252, obsd 160.1244.

6-(2-Acetoxy-4-phenyl-*trans*-3-butenyl)-6-methylfulvene(7). Reaction of 234 mg (1.00 mmol) of 1,1-diacetoxy-3-phenyl-2-propene with 1.20 mmol of the anion of **1** in the presence of 9.2 mg (0.016 mmol) of $Pd(dba)_2$ and 8.7 mg (0.033 mmol) of PPh_3 in 7 mL of THF for 2 h at ambient temperature, gave after chromatography (hexanes-ethyl acetate, 9:1), 135 mg (0.48 mmol, 48%) of **7** as a yellow oil. ^1H NMR (90 MHz) δ 7.32 (m, 5H), 6.65 (d, 1H, J = 16.4 Hz), 6.48 (m, 4H), 6.16 (dd, 1H, J = 15.9 and 6.9 Hz), 3.07 (dd, 1H, J = 13.0 and 7.9 Hz), 2.72 (dd, 1H, J = 13.5, 5.9 Hz), 2.24 (s, 3H), 1.97 (s, 3H); ^{13}C NMR (22.5 MHz) δ 170.1 (s), 152.7 (s), 146.5 (s), 136.1 (s), 132.7 (d), 131.4 (d), 131.2 (d), 128.6 (d, 3C),128.1 (d), 126.8 (d), 126.6 (d, 2C), 120.8 (d), 72.9 (d), 42.0 (t), 21.7 (q), 21.0 (q, 2C); IR (film) 3060, 3030, 2930, 1730, 1675, 1635, 1450, 1370, 1230, 1020, 965, 950, 895 cm^{-1}; GLC-MS or GLC-HRMS could not be obtained.[40]

6-(5-Acetoxy-*trans*-3-pentenyl)-6-methylfulvene(8) and 6-(2-Acetoxymethyl-3-butenyl)-6-methylfulvene(9). Reaction of 790 mg (5.00 mmol) of *trans*-1-acetoxy-4-chloro-2-butene with 5.30 mmol

of the anion of **1** in the presence of 121 mg (0.21 mmol) of $Pd(dba)_2$ and 110 mg (0.42 mmol) of PPh_3 in 28 mL THF for 1 h at ambient temperature, gave after chromatography (hexanes-EtOAc, 9:1), 497 mg (2.28 mmol, 46%) of a 3:1 mixture of **8** and **9** as a yellow oil. Spectroscopic data from a 3:1 mixture of **8** and **9**: ^{1}H NMR (90 MHz, **9**) δ 6.48 (s, 4H), 5.60 (m, 1H), 5.14 (d, J = 4.2 Hz, 1H), 4.99 (m, 1H), 4.03 (d, 2H, J = 5.9 Hz), 2.78-2.35 (m, 3H), 2.18 (s, 3H), 2.03 (s, 3H); ^{1}H NMR (90 MHz, **8**) δ 6.48 (s, 4H), 5.60 (m, 2H), 4.60 (d, 2H, J = 5.6 Hz), 2.78-2.35 (m, 4H), 2.20 (s, 3H), 2.04 (s, 3H); Partial ^{13}C NMR (22.5 MHz) δ 151.5 (s), 149.5 (s), 143.0 (s), 142.4 (d), 138.8, 137.6, 133.4 (d), 131.0 (d), 130.9 (d), 130.8 (d), 124.3 (d), 130.6 (d), 120.2 (d), 116.6 (t), 66.5 (t), 64.8 (t), 59.9 (t), 50.3 (d), 41.9 (q), 38.4 (q), 36.2 (t), 26.8 (t), 20.8 (q), 20.6 (q); IR (film) 3070, 3020, 2940, 1730 (CO), 1630, 1440, 1365, 1225, 1020, 760 cm^{-1}; GLC-MS (EI, **8**) *m/z* 158 (M^+-HOAc); GLC-MS (EI, **9**) m/z 158 (M^+-HOAc); GLC-HRMS (EI, **8**) exact mass calcd for $C_{14}H_{18}O_2$ *m/z* 218.1307, obsd 218.1312; GLC-HRMS (EI, **9**) exact mass calcd for $C_{14}H_{18}O_2$ *m/z* 218.1307, obsd 218.1305.

6-(*trans*-6-Acetoxy-2-cyclohexenylmethyl)-6-methylfulvene(10) and 6-(*trans*-4-Acetoxy-2-cyclohexenylmethyl)-6-methylfulvene(11). Reaction of 174 mg (1.00 mmol) of *cis*-1-acetoxy-4-chloro-2-cyclohexene with 1.12 mmol of the anion of **1** in the presence of 12 mg (0.021 mmol) of $Pd(dba)_2$ and 8 mg (0.020 mmol) of 1,2-bis(diphenylphosphino)ethane[41] in 7 mL THF for 30 min. at 0 °C, gave after chromatography (hexanes-EtOAc, 8:2), 203 mg (0.83 mmol, 83%) of a 10:7 mixture of **10** and **11** as a yellow oil. Samples for analyses were obtained by HPLC using hexanes-diethyl ether (97:3) as eluent.

Spectral data for **10**: ^{1}H NMR (400 MHz) δ 6.48 (m, 4H), 5.77 (d with further fine splitting, J = 10 Hz, 1H), 5.68 (dd with further fine splitting, J = 10 and 3 Hz, 1H), 5.31 (m, 1H), 2.52 (m, 3H), 2.22 (s, 3H), 2.08 (m, 1H), 2.05 (s, 3H), 1.83 (m, 1H), 1.59 (m, 1H), 1.36 (m, 1H); ^{13}C NMR (100 MHz) δ 170.8, 150.3, 144.2, 135.1, 131.2, 131.0, 126.9 (2C), 120.6, 69.2, 42.5, 34.3, 27.3, 23.4, 21.4, 21.0; IR (film) 2940, 2860, 1725, 1630, 1440, 1370, 1240, 1020, 770 cm^{-1}; GLC-MS (EI) *m/z* 184 (M^+-HOAc); HRMS (EI) exact mass calcd for $C_{16}H_{20}O_2$ *m/z* 244.1463, obsd 244.1445.

Spectral data for **11**: ^{1}H NMR (400 MHz) δ 6.46 (m, 4H), 5.71 (ddd, J = 10.0, 5.5, and 2.0 Hz, 1H), 5.44 (ddd, J = 10.0, 4.5, and 2.4 Hz, 1H), 4.75 (ddd, J = 9.5, 6.8, and 2.9 Hz, 1H), 2.67 (dd, J = 11.2 and 6.2 Hz, 1H), 2.62 (m, 1H), 2.51 (dd, J = 11.3 and 7.4 Hz, 1H), 2.24 (s, 3H), 2.16 (m, 2H), 1.99 (s, 3H), partly overlapping 1.98 (m, 1H), 1.68 (m, 1H); ^{13}C NMR (100 MHz) δ 170.7, 150.4, 144.1, 131.2, 130.9, 127.5, 127.2, 120.6, 120.6, 74.2, 40.8, 39.2, 26.4, 23.5, 21.2, 20.9. IR (film) 3060, 3020, 2910, 1720, 1625, 1430, 1360, 1230, 1020, 760 cm^{-1}; GLC-MS (EI) *m/z* 184 (M^+-HOAc); HRMS (EI) exact mass calcd for $C_{16}H_{20}O_2$ *m/z* 244.1463, obsd 244.1485.

***trans*-1-Acetoxy-4-(1-carbomethoxy-2-oxo-1-propyl)-2-cyclohexene(16).** Sodium hydride, 0.45 g (15.0 mmol, 80%) was washed with a few mL of pentane and dried on a high-vacuum pump. The hydride was suspended in 10 mL of THF and a solution of 1.74 g (15.0 mmol) of methyl acetoacetate in 6 mL of THF was added. After all the sodium hydride was consumed, the solvent was removed using a vacuum pump followed by addition of 10 mL of acetonitrile to the solid residue. A solution of 1.00 g (5.73 mmol) of *cis*-1-acetoxy-4-chloro-2-cyclohexene in 10 mL of acetonitrile was added via pipette under a positive flow of

nitrogen. The reaction mixture was heated at reflux for 16 h, cooled to ambient temperature and treated with 1.06 g (12.6 mmol) of sodium bicarbonate. After stirring for 3 h, 75 mL of diethyl ether was added, the formed precipitate was filtered off through a Celite pad and the pad was washed with 30 mL of diethyl ether. Removal of the solvents on a rotary evaporator gave a brown oil. The crude product was chromatographed on a 2.5 x 25 cm column eluted with, in sequence, hexanes-EtOAc (19:1), hexanes-EtOAc (8:2), hexanes-EtOAc (7:3) to afford 1.226 g (4.83 mmol, 85%, isomeric purity by GLC > 97:3) of **16** as a colorless oil. ^{1}H NMR (90 MHz) δ 5.70 (s, 2H), 5.25 (m, 1H), 3.74 (s, 3H), 3.38 (d, J = 10.2 Hz, 1H), 2.99 (m, 1H), 2.24 (s, 3H), 2.03 (s, 3H) superimposed on 2.1-1.4 (m, 4H); ^{13}C NMR (22.5 MHz) δ 201.1 (s), 170.0 (s), 168.3 (s), 131.4 (d), 131.2 (d), 128.4 (d), 128.1 (d), 68.1 (d, C1), 63.3 (d), 63.2 (d), 51.9 (q, OMe), 34.2 (d), 29.4 (q), 29.3 (q), 26.7 (t), 23.8 (t), 23.5 (t), 20.7 (q); IR (film) 3030, 3000, 2950, 2870, 1710, 1430, 1360, 1240, 1155, 1025, 910, 730, 645 cm^{-1}; Anal. Calcd for $C_{13}H_{18}O_5$: C, 61.42; H 7.09. Found: C, 61.38; H, 7.10.

***trans*-1-Acetoxy-4-(2-oxo-1-propyl)-2-cyclohexene(17) and *trans*-Methyl 2-methyl-3a,4,5,7a-tetrahydro-3-benzofuranecarboxylate(18).** A mixture of 508 mg (2.00 mmol) of **16**, 424 mg (10.00 mmol) of LiCl, and 180 mg (10.00 mmol) of water in 5 mL of dimethyl sulfoxide was heated to 175 °C for 45 min. The reaction mixture was poured into 40 g of ice and extracted with first two 20 mL portions of pentane then with 20 mL of diethyl ether. The combined organic phase was dried ($MgSO_4$) and the solvent was removed on a rotary evaporator to give a yellow oil. The oil was chromatographed on a 3 x 15 cm column eluted with hexanes - EtOAc (9:1) affording 30 mg (0.15 mmol, 8%) of **18** and 237 mg (1.21 mmol, 60%) of **17** both as faint yellow oils. The acetate **17** was >96% isomerically pure (GLC). Spectral data for **18** was in complete accordance with literature values.[42] Spectral data for **17**: ^{1}H NMR (90 MHz) δ 5.69 (s, 2H), 5.24 (m, 1H), 2.61 (m, 1H), 2.45 (m, 2H), 2.15 (s, 3H), 2.05 (s, 3H), partially overlapping 2.05-1.21 (m, 4H); ^{13}C NMR (22.5 MHz) δ 207.2 (s), 170.6 (s), 134.8 (d), 126.9 (d), 68.9 (d), 48.8 (t), 30.7 (d, C4), 30.4 (q), 27.2 (t), 26.1 (t), 21.2 (q); IR (film) 3020, 2910, 2860, 1710, 1365, 1240, 1150, 1020, 900, 735 cm^{-1}; GLC-MS (EI) *m/z* 138 (M^+-CH_3COCH_3), 136 (M^+-HOAc); HRMS (CI, CH_4) exact mass calcd for MH^+ $C_{11}H_{17}O_3$ *m/z* 197.1177, obsd 197.1140.

6-(*trans*-4-Acetoxy-2-cyclohexenylmethyl)-6-methylfulvene(10) and 6-(*trans*-4-Hydroxy-2-cyclohexenylmethyl)-6-methylfulvene(19). To a solution of 196 mg (1.00 mmol) of **17** and 165 mg (2.50 mmol) of freshly distilled 1,3-cyclopentadiene in 10 mL of methanol was added 209 μL (1.50 mmol) of pyrrolidine via syringe. After 24 h at ambient temperature, an additional 165 mg (2.50 mmol) of 1,3-cyclopentadiene and 418 μL (3.00 mmol) of pyrrolidine was added.[43] The mixture was stirred for 24 h whereafter 1 mL of acetic acid was added to the formed yellow solution. After stirring for 15 min., the solvent was removed on a rotary evaporator. The crude yellow oil was chromatographed on a 20 x 2.5 cm column eluted, in sequence, with hexanes then hexanes - EtOAc (9:1) and finally hexanes-EtOAc (7:3) to give 43 mg (0.17 mmol, 17%) of **10** as a yellow oil together with 117 mg (0.57 mmol, 57%) of **19**. The product was in all respects (GLC-MS, ^{1}H NMR, and ^{13}C NMR) identical to **10** prepared by the palladium-catalyzed reaction described above.

Spectral data for **19**: IR (film) 3360, 2930, 2855, 1700, 1370, 1260, 1055, 1015, 765 cm^{-1}; ^1H NMR (90 MHz) δ 6.46 (m, 4H), 5.68 (br s, 2H), 4.23 (t, J = 6.9, 1H), 2.52 (m, 3H), 2.47 (s, 2H), 2.20 (s, 3H), 2.2-1.2 (m, 6H); ^{13}C NMR (22.5 MHz) δ 150.7 (s), 133.2 (d), 131.1 (d, 2C), 130.8 (d), 120.6 (d, 2C), 66.6 (d), 42.7 (t), 34,5 (d), 31.5 (t), 26.9 (t), 20.9 (q); HRMS (EI) exact mass calcd for $C_{14}H_{18}O$ *m/z* 202.1358, obsd 202.1360.

The alcohol **19** undergoes polymerization rapidly and was immediately converted to the acetate **10** by the following reaction: Treatment of 56 mg (0.28 mmol) of **19** with 45 mg (0.37 mmol) of 4-(*N,N*-dimethylamino)pyridine and 29 μL (0.31 mmol) of acetic anhydride in 10 mL of diethyl ether at 0 °C for 4 h gave a golden-yellow solution. The ether solution was washed with 10 mL of hydrochloric acid (10% aq.) followed by 10 mL of saturated aqueous sodium bicarbonate. The organic phase was dried ($MgSO_4$) and the solvent was removed on a rotary evaporator. The resulting gummy yellow residue was chromatographed eluting with hexanes-EtOAc (9:1) to give after solvent removal, 25 mg (0.10 mmol, 36%) of **10** as a yellow oil.

***trans*-6-Hydroxy-1-(2-propenyl)-2-cyclohexene(20).** A solution of 1120 μL (13.83 mmol) of 3-chloropropene dissolved in 25 mL of ether was added dropvise over a 10 min period, to a flame-dried airless flask containing 347 mg (14.28 mmol) of magnesium and a few iodine crystals. After 30 min, 1147 mg (11.94 mmol) of 1,3-cyclohexadiene monoepoxide dissolved in 15 mL of ether was added to the grignard reagent. The mixture was stirred for 4 h, 25 mL of 10% HCl (aq) was added the phases was separated and the organic phase was washed with water (2 x 25 ml). The organic phase was dried with $MgSO_4$ followed by removal of the solvent on a rotary evaporator. The residue was chromatographed on a 15 x 2 cm column eluted with first 100 mL of hexanes-EtOAc (8:2) followed by hexanes-EtOAc (7:3) to give 667 mg (4.83 mmol, 40%) of **20** as a colorless oil. ^1H NMR (90 MHz) δ 6.05-5.43 (m, 3H), 5.17-5.00 (m, 2H), 3.63 (m, 1H); ^{13}C NMR (22.5 MHz) δ 136.6 (d), 128.3 (d), 126.6 (d), 116.4 (t), 71.0 (d), 43.4 (d), 37.4 (t), 30.0 (t), 23.9 (t); IR (film) 3350, 3070, 3020, 2910, 1445, 1045, 910 cm^{-1}; HRMS (EI) exact mass calcd for $C_9H_{14}O$ *m/z* 138.1045, obsd 138.1047.

***trans*-6-Acetoxy-1-(2-propenyl)-2-cyclohexene(21).**

To a 0 °C solution of 653 mg (4.73 mmol) of **20**, 388 mL (4.80 mmol) of pyridine, and 119 mg (0.98 mmol) of 4-(*N,N*-dimethylamino)-pyridine in 30 mL of diethyl ether was added 500 μL (5.30 mmol) of acetic anhydride via syringe. The solution was stirred for 2 h at 0 °C followed by 1 h at ambient temperature, after which 25 mL of Et_2O and 10 mL of water was added followed by separation of the phases. The water phase was extracted with two 15 mL portion of ether. The combined organic phase was dried with $MgSO_4$ followed by removal of solvent on a rotary evaporator to give a faint yellow oil. The crude oil was chromatographed on a 15 x 2 cm column eluted with hexanes - EtOAc (9:1) to give 635 mg (3.57 mmol, 75%) of **21** as a colorless oil. ^1H NMR (90 MHz) δ 6.01-5.44 (m, 3H), 5.10 (br s, 1H), 4.95 (br s, 1H), 4.77 (ddd, J = 11.2, 6.6 and 3.6 Hz, 1H), 2.05 (s, 3H), superimposed on 2.39-1.56 (m, 7H); ^{13}C NMR (22.5 MHz) δ 170.6 (s), 135.8 (d), 127.9 (d), 126.7 (d), 116.6 (t), 73.4 (d), 40.1 (d), 37.1 (t), 26.5 (t), 23.5 (t), 21.6 (q); IR (film) 3070, 3020, 2930, 2840, 1720, 1370, 1240, 1030, 915 cm^{-1}; HRMS (EI) exact mass calcd for $C_9H_{12}O$ (M^+-CH_3COOH)[44] *m/z* 120.0939, obsd 120.0932.

***trans*-7-Acetoxy-1-(2-oxo-1-propyl)-2-cyclohexene(22).** A slow stream of oxygen was bubbled through a slurry of 380 mg (3.84 mmol) of copper chloride and 137 mg (0.77 mmol) of palladium dichloride in 4 mL of 15% aqueous DMF under stirring. After 1 h, 636 mg (3.57 mmol) of **21** dissolved in 1.5 mL of 15% aqueous DMF was added. The reaction mixture was stirred for 20 h diluted with 15 mL of water and extracted twice with 20 mL of diethyl ether. The organic phase was dried with $MgSO_4$ followed by removal of solvent on a rotary evaporator to give a faint yellow oil. The crude oil was chromatographed on a 15 x 2 cm column eluted with hexanes then hexanes - EtOAc (9:1) to give 476 mg (2.45 mmol, 69%) of **22** as a colorless oil. ^{1}H NMR (90 MHz) δ 5.69 (br dd, J = 10.4 and 1.8 Hz, 1H), 5.41 (br d, J = 10.3 Hz, 1H), 4.70 (ddd, J = 9.4, 7.5, and 3.4 Hz, 1H, H1), 2.79 (m, 1H), 2.46 (m, 2H), 2.15 (s, 3H), 2.04 (s, 3H), partly superimposed on 2.2-1.7 (m, 4H); ^{13}C NMR (22.5 MHz) δ 207.1 (s), 170.0 (s), 127.6 (d), 127.1 (d), 73.6 (d, C1), 47.0 (t), 36.6 (d), 30.2 (q), 26.7 (t), 23.6 (t), 21.2 (q); IR (film) 3020, 2920, 2840, 1710, 1415, 1360, 1240, 1030, 740, 685 cm^{-1}; GLC-MS (EI) *m/z* 136 (M^+-HOAc); HRMS (EI) exact mass calcd for $C_{11}H_{15}O_3$ (M^+-H) *m/z* 195.1021, obsd 195.1021, $C_9H_{12}O_1$ (M^+-CH_3COOH) *m/z* 136.0881, obsd 136.0883.

6-(*trans*-6-acetoxy-2-cyclohexenylmethyl)-6-methylfulvene(11). To a solution of 76 mg (0.39 mmol) of **22** and 37 mg (0.56 mmol) of freshly distilled 1,3-cyclopentadiene in 30 mL of methanol was added 30 μL (0.36 mmol) of pyrrolidine via syringe. After stirring for 2 h at ambient temperature, 100 μL (1.77 mmol) of acetic acid was added to the resulting yellow solution. After stirring for 15 min, the yellow solution solution was washed with water (3 x 30 mL), the organic phase dried with $MgSO_4$ followed by solvent removal on a rotary evaporator. The crude yellow oil was chromatographed on a 15 x 2 cm column eluted with hexanes - EtOAc (8:2) to give 48 mg (0.20 mmol, 51%) of **11** as a yellow oil. The product was in all respects (GLC-MS, ^{1}H NMR, and ^{13}C NMR) identical to **11** prepared by the palladium-catalyzed reaction described above.

6-(3-Butenyl)-6-(1-methylethyl)fulvene(25). Reaction as above of 1.20 mL (15.0 mmol) of 3-chloro-1-propene with 10.0 mmol of the anion of 6-methyl-6-(1-methylethyl)fulvene (**24**) in the presence of 230 mg (0.40 mmol) of $Pd(dba)_2$ and 210 mg (0.80 mmol) of PPh_3 in 24 mL of THF for 90 min. at ambient temperature, gave after chromatography (pentanes), 1205 mg (6.93 mmol, 93%) of **25** as a yellow oil. ^{1}H NMR (90 MHz) δ 6.47 (m, 4H), 6.12-5.69 (m, 1H), 5.11 (br d, 1H, J = 9.6 Hz), 4.96 (m, 1H), 3.30 (quintet, 1H, J = 7.1 Hz), 2.68-2.17 (m, 4H), 1.07 (d, 6H); ^{13}C NMR (22.5 MHz) δ 161.7 (s), 142.0 (s), 137.8 (d), 130.9 (d), 130.3 (d), 121.1 (d), 119.8 (d), 114.7 (t), 37.2 (t), 33.9 (d), 30.1 (t), 22.0 (q); IR (film) 3070, 2970, 2870, 1615, 1460, 1365, 1085, 995, 910, 880, 770, 690 cm^{-1}; GLC-MS (EI) *m/z* 174 (M^+); HRMS (EI) exact mass calcd for $C_{13}H_{18}$ *m/z* 174.1409, obsd 174.1403.

6,6-(6-(2-Propenyl))tetramethylenefulvene(27). Reaction as above of 244 μL (3.00 mmol) of 3-chloro-1-propene with 2.00 mmol of the anion of tetramethylenefulvene (**26**) in the presence of 46 mg (0.08 mmol) of $Pd(dba)_2$ and 42 mg (0.16 mmol) of PPh_3 in 10 mL of THF for 30 min. at ambient temperature, gave after chromatography (pentanes), 166 mg (0.97 mmol, 48%) of **27** as a yellow oil. ^{1}H NMR (90 MHz) δ 6.40 (m, 4H), 6.03-5.58 (m, 1H), 5.11 (br s, 1H), 4.96 (br d, 1H, J = 12 Hz), 3.34-3.01 (br m, 1H), 2.81 (br m, 2H), 2.40-2.23 (br m, 2H), 1.91-1.68 (br m, 4H); ^{13}C NMR (22.5 MHz) δ 164.5 (s), 138.6 (s), 136.5 (d), 130.3 (d), 130.0 (d), 121.6 (d), 121.1 (d), 116.2 (t), 43.9 (d), 41.3 (t), 32.5 (t), 30.6 (t), 23.4 (t); IR (film)

3070, 2960, 2870, 1640, 1460, 1365, 1080, 9995, 910, 765, 735, 635 cm^{-1}; GLC-MS (EI) *m/z* 172 (M^+); HRMS (EI) exact mass calcd for $C_{13}H_{18}$ *m/z* 172.1252, obsd 172.1258.

6-(3-Butenyl)-6-phenylfulvene(29). Reaction as above of 815 μL (6.80 mmol) of 3-chloro-1-propene with 10.0 mmol of the anion of 6-methyl-6-phenylfulvene (**28**) in the presence of 155 mg (0.27 mmol) of $Pd(dba)_2$ and 144 mg (0.54 mmol) of PPh_3 in 18 mL of THF for 90 min. at ambient temperature, gave after chromatography (hexanes), 975 mg (4.69 mmol, 69%) of **29** as a red oil. ^1H NMR (90 MHz) δ 7.35 (s, 5H), 6.51 (m, 3H), 6.14 (m, 1H), 5.94-5.47 (m, 1H), 5.03 (d, 1H, *J* = 4.7 Hz), 4.87 (s, 1H), 3.00 (t, 2H, *J* =7.5 Hz), 2.17 (q, 2H, *J* =7.2 Hz); ^{13}C NMR (22.5 MHz) δ 153.3 (s), 143.7 (s), 140.5 (s), 137.3 (d), 132.0 (d), 131.6 (d), 128.1 (d), 127.7 (d), 123.8 (d), 120.8 (d), 115.2 (t), 35.6 (t), 33.6 (t); IR (film) 3080, 2970, 2920, 1605, 1435, 1360, 990, 920, 900, 770, 705 cm^{-1}; GLC-MS (EI) *m/z* 208 (M^+); HRMS (EI) exact mass calcd for $C_{16}H_{16}$ *m/z* 208.1252, obsd 208.1236.

6-(1-Methyl-3-butenyl)fulvene(31). Reaction as above of 815 μL (3.00 mmol) of 3-chloro-1-propene with 2.00 mmol of the anion of 6-ethylfulvene (**30**) in the presence of 46 mg (0.08 mmol) of $Pd(dba)_2$ and 42 mg (0.16 mmol) of PPh_3 in 16 mL of THF for 90 min. at ambient temperature, gave after chromatography (pentanes), 180 mg (1.23 mmol, 62%) of **31** as a yellow oil. ^1H NMR (90 MHz) δ 6.45 (m, 2H), 6.19 (m, 2H), 5.76 (m, 1H), 5.11-4.93 (m, 2H), 3.29-2.64 (m, 1H), 2.20 (t, 2H, *J* = 6.6 Hz), 1.13 (d, 3H); ^{13}C NMR (22.5 MHz) δ 147.6, 144.6, 136.0, 133.1, 130.8, 125.8, 119.4, 116.5, 41.4, 35.6, 20.68; IR (film) 3070, 2960, 2920, 1635, 1450, 1375, 1335, 1075, 990, 955, 910, 890, 765, 730, 610 cm^{-1}; GLC-MS (EI) *m/z* 146 (M^+); HRMS (EI) exact mass calcd for $C_{11}H_{14}$ *m/z* 146.1096, obsd 146.1095.

6-(1,1-Dimethyl-3-butenyl)fulvene(33). Reaction as above of 1.20 mL (15.0 mmol) of 3-chloro-1-propene with 10.0 mmol of the anion of 6-(1-methylethyl)fulvene (**32**) in the presence of 230 mg (0.40 mmol) of $Pd(dba)_2$ and 210 mg (0.80 mmol) of PPh_3 in 24 mL of THF for 90 min. at ambient temperature, gave after chromatography (pentanes), 365 mg (2.28 mmol, 23%) of **33** as a yellow oil. ^1H NMR (90 MHz) δ 6.62 (m, 2H), 6.40 (m, 2H), 6.16 (m, 1H), 5.77 (m, 1H), 5.07 (m, 2H), 2.27 (d, 2H, *J* = 7.1 Hz), 1.28 (s, 6H); ^{13}C NMR (22.5 MHz) δ 152.3 (d), 143.4 (s), 136.0 (d), 134.3 (d), 128.6 (d), 128.4 (d), 120.1 (d), 117.6 (t), 41.4 (d), 39.0 (s), 20.7 (q, 2C); IR (film) 3060, 2950, 2920, 2860, 1625, 1455, 1075, 990, 900, 890, 760, 725, 640, 610 cm^{-1} GLC-MS (EI) *m/z* 160 (M^+); HRMS (EI) exact mass calcd for $C_{12}H_{16}$ *m/z* 160.1252, obsd 160.1268.

Acknowledgement Startup funds to BCS provided by the University of South Alabama and funding by the Swedish Natural Science Research Council is acknowledged.

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(*Received in USA* 16 *March* 1993; *accepted* 7 *October* 1993)