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A New Synthesis of Substituted Fulvenes

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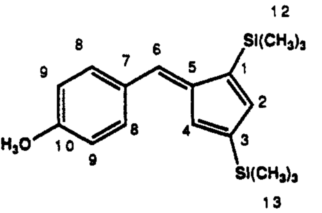
Abstract: A new fulvene synthesis results from the palladium-catalyzed [2 + 2 + 2] annulation of 1 mol of a β-substituted vinyl iodide and 2 mol of a monosubstituted acetylene. This variant of the Heck reaction tolerates a wide range of substrate substituents with the best results obtained by using the catalyst, $Pd(CH_3CN)_2Cl_2$. Addition of $Cu^{I}I$ to the reaction affords high yields of 1,3-enyne and no fulvene. A [6.5]spiro system is formed from 4-*tert*-butyl-1-cyclohexenyl triflate and a biphenyl is formed from 1-aryl-1-bromoethene under these conditions. A mechanism for this novel fulvene synthesis is proposed.

During the past 15 years, the inter-, and more recently the intra-, molecular palladium-catalyzed arylation and alkenylation of alkenes (the Heck reaction[1]) have established themselves as powerful tools for the preparation of heterocycles[2] and carbocycles.[3] While the intermolecular arylation and alkenylation of alkynes have found wide application,[1] only recently have the corresponding intramolecular versions been disclosed from several laboratories.[4] Here we report our results on a novel palladium-catalyzed [2 + 2 + 2] annulation of a vinyl iodide to yield a substituted fulvene.

Our new fulvene synthesis is outlined in Scheme I. In our initial investigation, exposure of 2-(4-methoxyphenyl)-1-iodoethene (**1**, E:Z = 95:5) to trimethylsilylacetylene (2.5 equiv) and 5 mol % of $Pd(CH_3CN)_2Cl_2$ in *N*,*N*-dimethylformamide gave no sign of the expected trimethylsilylenyne **2**. Instead an orange solid, fulvene **3**, was obtained, the structure of which was rigorously established by chemical transformations and extensive NMR studies. Thus, treatment of **3** with 4-toluenesulfinic acid[6] gave the corresponding desilylated fulvene **4**, which was identical with an authentic sample obtained via an alternative synthesis (Scheme II). Protodesilylation of **3** occurs in a stepwise fashion via the monodesilylated fulvene **5**. Hydrogenation of **3** using 10% palladium on carbon gave the expected bis(trimethylsilyl)cyclopentane derivative **6**. Structural confirmation of **3** was obtained by a combination of HETCOR,[8-10] XCORFE,[11] and NOE[12] experiments, and the results are summarized in Tables I and II. Table I shows the ^{13}C and ^{1}H chemical shifts and the observed long range ^{13}C–^{1}H connectivities of **3**. Table II shows the ^{1}H homonuclear NOEs observed when protons 4, 6, 12, and 13 of compound **3** were irradiated. The alternative regiosomer (**3**, but TMS at C-2 and C-4) is inconsistent with the data from the NOE experiments. Thus, there was no NOE observed between H-12 and H-8 but rather between H-4 and H-8 and between H-12 and H-6.

Table I. ^{13}C Chemical Shifts, Direct and Long-Range ^{1}H Connectivities of **3**



atom	^{13}C chemical shifts	^{1}H chemical shifts	^{1}H correlations (obsd) long range
1	138.19		H-6, H-12, H-2
2	144.8	6.81	H-4
3	148.35		H-2, H-4
4	132.94	6.99	H-6
5	149.0		H-4, H-2
6	137.96	7.27	H-8
7	129.9		H-9
8	132.51	7.53	H-6
9	114.21	6.94	
10	160.4		H-8, H-11
11	55.3	3.85	
12	0.5	0.19	
13	−1.11	0.28	

Table II. ^{1}H NOE's for **3**[a]

^{1}H (irradiated)	NOE (obsd)	^{1}H (irradiated)	NOE (obsd)
H-4	H-8	H-12	H-2, H-6
H-6	H-8	H-13	H-2, H-4

[a] Numbering of ^{1}H is the same as used in Table I.

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(1) For a review of the Heck reaction, see: (a) Heck, R. F. *Acc. Chem. Res.* **1979**, *12*, 146. (b) Heck, R. F. *Org. React. N.Y.* **1982**, *27*, 345. (c) Heck, R. F. *Palladium Reagents in Organic Synthesis*; Academic Press: New York, 1985.

(2) For recent papers not cited in ref 1c, see: (a) Kasahara, A.; Izumi, T.; T.; Murakami, S.; Yanai, H.; Takatori, M. *Bull. Chem. Soc. Jpn.* **1986**, *59*, 927. (b) Grigg, R.; Sridharan, V.; Stevenson, P.; Worakun, T. *J. Chem. Soc., Chem. Commun.* **1986**, 1697. (c) Abelman, M. M.; Oh, T.; Overman, L. E. *J. Org. Chem.* **1987**, *52*, 4133. (d) Larock, R. C.; Babu, S. *Tetrahedron Lett.* **1987**, *28*, 5291. (e) Burns, B.; Grigg, R.; Ratananukul, P.; Sridharan, V.; Stevenson, P.; Worakun, T. *Tetrahedron Lett.* **1988**, *29*, 4329. (f) Arcadi, A.; Cacchi, S.; Marinelli, F. *Tetrahedron Lett.* **1989**, *30*, 2581.

(3) Recent publications include the following: (a) Narula, C. K.; Mak, K. T.; Heck, R. F. *J. Org. Chem.* **1983**, *48*, 2792. (b) Grigg, R.; Stevenson, P.; Worakun, T. *J. Chem. Soc., Chem. Commun.* **1984**, 1073. (c) Tour, J. M.; Negishi, E. *J. Am. Chem. Soc.* **1985**, *107*, 8289. (d) Negishi, E.; Zhang, Y.; O'Connor, B. *Tetrahedron Lett.* **1988**, *29*, 2915. (e) Larock, R. C.; Song, H.; Baker, B. E.; Gong, W. H. *Tetrahedron Lett.* **1988**, *29*, 2919. (f) O'Connor, B.; Zhang, Y.; Negishi, E. *Tetrahedron Lett.* **1988**, *29*, 3903. (g) Grigg, R.; Stevenson, P.; Worakun, T. *Tetrahedron* **1988**, *44*, 2033. (h) *Ibid.* **1988**, *44*, 2049. (i) Zhang, Y.; O'Connor, B.; Negishi, E. *J. Org. Chem.* **1988**, *53*, 5588. (j) Larock, R. C.; Gong, W. H. *J. Org. Chem.* **1989**, *54*, 2047.

(4) Recent publications include the following: (a) Wu, G.; Geib, S. J.; Rheingold, A. L.; Heck, R. F. *J. Org. Chem.* **1988**, *53*, 3238. (b) Arcadi, A.; Cacchi, S.; Marinelli, F. *Tetrahedron* **1985**, *41*, 5121. (c) Burns, B.; Grigg, R.; Sridharan, V.; Worakun, T. *Tetrahedron Lett.* **1988**, *29*, 4325. (d) Trost, B. M.; Lee, D. C. *J. Am. Chem. Soc.* **1988**, *110*, 7255. (e) Abelman, M. M.; Overman, L. E. *J. Am. Chem. Soc.* **1988**, *110*, 2328. (f) Carpenter, N. E.; Kucera, D. J.; Overman, L. E. *J. Org. Chem.* **1989**, *54*, 5846. (g) Zhang, Y.; Negishi, E. *J. Am. Chem. Soc.* **1989**, *111*, 3454. (h) Wu, G.; Lamaty, F.; Negishi, E. *J. Org. Chem.* **1989**, *54*, 2507.

(5) Prepared from 4-methoxybenzaldehyde according to Takai, K.; Nitta, K.; Utimoto, K. *J. Am. Chem. Soc.* **1986**, *108*, 7408.

(6) Buchi, G.; Wuest, H. *Tetrahedron Lett.* **1977**, 4305.

(7) Otter, A.; Muhle, H.; Neuenschwander, M.; Kellerhals, H. P. *Helv. Chim. Acta*, **1979**, *62*, 1626.

(8) Maudsley, A. A.; Ernst, R. R. *Chem. Phys. Lett.* **1977**, *50*, 368.

(9) Bodenhausen, G.; Freeman, R. *J. Magn. Reson.* **1977**, *28*, 471.

(10) Maudsley, A. A.; Muller, L.; Ernst, R. R. *J. Magn. Reson.* **1977**, *28*, 463.

(11) Reynolds, W. F.; Hughes, D. W.; Perpick-Dumont, M. *J. Magn. Reson.* **1985**, *63*, 413–417.

(12) Sanders, J. K. M.; Mersh, J. D. *Prog. NMR Spectrosc.* **1982**, *15*, 353.

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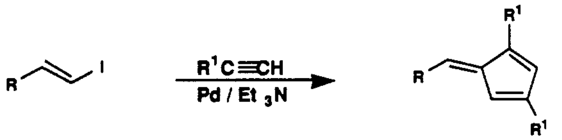
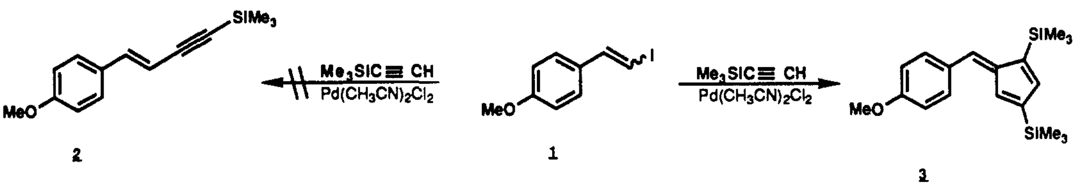
Table III. Synthesis of Substituted Fulvenes



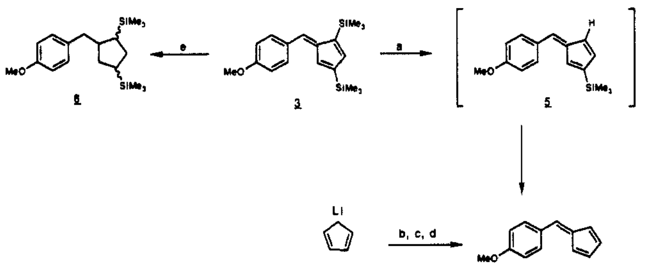
entry	halide[a] R	method[b]	products	yields,[c] %
1	Ph	A	**7**, R = Ph, R^1 = TMS	44
2	4-MeOPh (**1**)	A	**3**, R = 4-MeOPh, R^1 = TMS	46
3		A	**29**, R = 4-MeOPh, R^1 = Ph	18[d,e]
4		B	**30**, R = 4-MeOPh, R^1 = *n*-Pr	33
5		B	**31**, R = 4-MeOPh, R^1 = *t*-Bu	44
6		A	**32**, R = 4-MeOPh, R^1 = CH_2OH	12[d]
7	2-McPh (**25**)	A	**33**, R = 2-MePh, R^1 = TMS	54
8	2-naph (**26**)	A	**34**, R = 2-naph, R^1 = TMS	43
9	3-thienyl (**27**)	A	**35**, R = 3-thienyl, R^1 = TMS	44[f]
10	*n*-heptyl (**28**)	A	**36**, R = *n*-heptyl, R^1 = TMS	16[d,g]
			37, R = *n*-heptyl, R^1 = TMS/H	

[a] Except entries 1 and 10 the vinyl iodides were prepared from the corresponding aldehydes according to ref 5. Entries 1–7, 8, and 10 started with (*E*)-vinyl iodides. Entry 9 started with a mixture of *E*/*Z* isomers in a ratio of 9:1. [b] All reactions contained vinyl iodide, alkyne, and NEt_3 in a 1:2.5:1.2 ratio for 14 h (overnight): method A, $Pd(MeCN)_2Cl_2$ (5 mol %) in DMF at 25 °C; method B, $Pd(PPh_3)_2Cl_2$ (5 mol %) in CH_3CN at 100 °C. [c] Isolated yields of products purified by column chromatography on silica gel and recrystallization (if applicable). Yields were not optimized. [d] These fulvenes decomposed during purification. [e] This fulvene was not formed by using method B. [f] By using method B, **35** (7% yield) was contaminated by many other unidentified products. [g] The C-1 monotrimethylsilyl fulvene **37** (5% yield) was also isolated.

Scheme I



Scheme II[a]



[a] Reagents: a = 4-toluenesulfinic acid/CH_3CN/H_2O/heat; b = 4-methoxybenzaldehyde; c = methanesulfonyl chloride; d = triethylamine; e = H_2/10% palladium/C.

The novelty of this palladium-catalyzed alkynylation of an alkene to form the relatively inaccessible substituted fulvene[13] prompted us to investigate the scope of the reaction. As seen from Table III, the Pd-catalyzed reaction between a β-iodoalkene and an alkyne seems to be a general one and constitutes a new synthesis of substituted fulvenes. Typically, the reaction was executed with a vinyl iodide (1 equiv), an alkyne (2.5 equiv), NEt_3 (1.2 equiv), and $Pd(CH_3CN)_2Cl_2$ (5 mol %) in DMF/25 °C (method A). However, for less reactive alkynes (Table III, entries 4 and 5) more vigorous conditions (5 mol % $Pd(PPh_3)_2Cl_2$ in refluxing acetonitrile, method B) were required to complete the reaction. In general method A gave a better yield and fewer side products than method B. Yields of fulvene are approximately 40% except for those which decomposed during purification (Table III, entries 3 and 6). In one case, with an aliphatic vinyl iodide (Table III, entry 10), apart from the expected fulvene, the very labile monosilylated fulvenes (TMS groups at C-1 or at C-3) were also obtained.

Since the Pd-catalyzed coupling reaction[1c] can be dependent on the nature of the substrate, the catalyst, the solvent, and the presence of other transition-metal ions,[15] we have investigated the effect of these parameters, and the critical findings are summarized in Tables III and IV. A large number of halogenated substrates were examined. Vinyl iodides rather than the corresponding bromides (data not shown) are preferred substrates. Vinylidene dibromide (Table IV, entry 1), however, gave the corresponding vinylidene diyne as the only product. Likewise, α-bromostyrene (Table IV, entry 2), in the absence or presence of Cu^{I}I, gave the corresponding enyne. Under method C conditions without CuI, 5-phenyl-1-iodo-1-pentyne gave no sign of reaction (Table IV, entry 3). However, in the presence of Cu^{I}I (vide infra), this alkyne and 1-iodophenylacetylene were converted exclusively into 1,3-butadiynes (Table IV, entries 4 and 5). The structure of the alkyne partner was also varied. Of the six terminal alkynes examined, only 1-ethoxyacetylene gave none of the expected fulvene but instead yielded the "normal" Heck reaction coupled product 1,3-enyne (Table IV, entry 6). Likewise, alkynes disubstituted with silicon or tin gave only the 1,3-enyne (Table IV, entries 7 and 8). Using a large excess of the alkyne (Table III, entries 1, 4, and 5), up to 10 equiv, has no obvious effect on the yield of the fulvene (data not shown). Surprisingly, when only 1 equiv of the alkyne was used, the fulvene was also obtained, albeit in lower yield. The 1,3-enyne could not be detected.

Of the variations in catalysts examined (Table V) $Pd(CH_3CN)_2Cl_2$ gave the best results, probably due to the milder conditions

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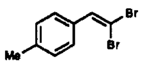
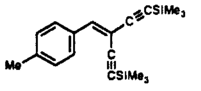
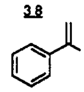
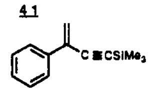
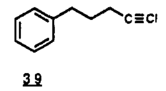
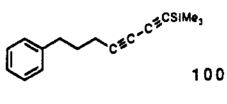
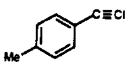
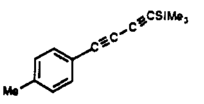
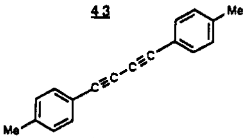
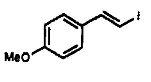
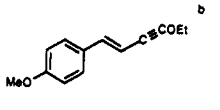
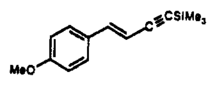
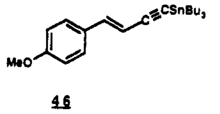
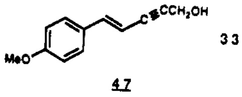
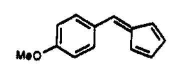
(13) To the best of our knowledge, these disilylated fulvenes (e.g., **3**) are not reported in the literature. For excellent review on fulvenes and related systems, see: (a) Neuenschwander, M. *Pure Appl. Chem.* **1986**, *58*, 55. (b) Yates, P. In *Advances in Allicyclic Chemistry*: Academic Press: New York, 1968; Vol. 2, p 59. (c) Bergman, E. D. *Chem. Rev.* **1968**, *68*, 41.

(14) Stille, J. K.; Simpson, J. H. *J. Am. Chem. Soc.* **1987**, *109*, 2138.

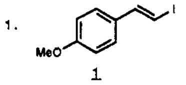
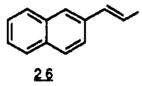
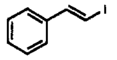
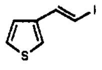
(15) The importance of Cu(I) ion in palladium-catalyzed alkynylation of alkene to form a 1,3-enyne is well documented, see: (a) Sonogashira, K.; Tohda, Y.; Hagihara, N. *Tetrahedron Lett.* **1975**, 4467. (b) Rossi, R.; Carpita, A.; Quirici, M. G.; Guadenzi, M. L. *Tetrahedron* **1982**, *38*, 631. (c) Cassar, L. *J. Organomet. Chem.* **1975**, *93*, 253. (d) Dieck, H. A.; Heck, F. R. *J. Organomet. Chem.* **1975**, *93*, 259. (e) For the effect of Ag(I)$^+$ on palladium-catalyzed coupling between vinyltrimethylsilane and aryl iodide, see: Karabelas, K.; Hallberg, A. *J. Org. Chem.* **1986**, *51*, 5286.

Table IV. Palladium-Catalyzed Coupling of Iodoalkenes/Iodoalkynes with Alkynes

entry	Haloalkene/ Haloalkyne	Alkyne	Method[a]	Product	Yield %[c]
1.	 38	Me$_3$SiC≡CH	B	 41	47
2.			C	 24	70
3.	 39		B	—	—
4.			C	 42	100
5.	 40		C	 43	38
				 44	35
6.	 1	EtOC≡CH	A	 45	—[b]
7.		Me$_3$SiC≡CSiMe$_3$	A	 10	37
8.		Bu$_3$SnC≡CSnBu$_3$	B	 46	19
9.		Me$_3$SiC≡CH	C	10	95
10.		HOCH$_2$C≡CH	C	 47	33
11.		Me$_3$SiC≡CH	D	 4	—

[a] Methods A and B are the same as those indicated in Table III: method C, Pd(PPh$_3$)$_2$Cl$_2$/Cu^{I}I (5 mol % each) in NEt$_3$ at 25 °C; method D, Pd(PPh$_3$)$_2$Cl$_2$ (5 mol %); Ag$_2$CO$_3$ (1 equiv based on vinyl halide), no NEt$_3$ in CH$_3$CN at 100 °C. [b] This enyne decomposed during purification. [c] Isolated yields of products purified by column chromatography on silica gel and recrystallized (if applicable). Yields were not optimized.

Table V. Effect of Varying the Palladium Catalyst on the Coupling Reaction

entry	Vinyl Iodide	Alkyne	Catalyst	% Yield of Fulvene
1.	 1	Me$_3$SiC≡CH	Pd(CH$_3$CN)$_2$Cl$_2$[a]	46
2.		Me$_3$SiC≡CH	Pd(PPh$_3$)$_2$Cl$_2$[b]	45[c]
3.		Me$_3$SiC≡CH	Pd(PPh$_3$)$_4$[a]	27
4.	 26	Me$_3$SiC≡CH	Pd(CH$_3$CN)$_2$Cl$_2$[a]	43
5.		Me$_3$SiC≡CH	Pd(OAc)$_2$/PPh$_3$ (1:1)[b]	30
6.		Me$_3$SiC≡CH	Pd(PPh$_3$)$_2$Cl$_2$[b]	16
7.		Me$_3$SiC≡CH	Pd(CH$_3$CN)$_2$Cl$_2$[a]	44
8.	 27	Me$_3$SiC≡CH	Pd(PPh$_3$)$_2$Cl$_2$[b]	5
9.		Me$_3$SiC≡CH	Pd(CH$_3$CN)$_2$Cl$_2$[b]	44

[a] Reaction was carried out by using method A as indicated in Table III, footnote *b*. [b] Reaction was carried out by using method B as indicated in Table III, footnote *b*. [c] No sign of reaction at 25 °C.

under which the catalyst was used (Table V, entries 6–9). However, for unreactive alkynes (Table III, entries 4 and 5), Pd(PPh$_3$)$_2$Cl$_2$ is recommended. The ratio of palladium/triphenylphosphine (stabilizing ligand) has some effect on the yield of the reaction. Thus, lowering the amount of triphenylphosphine (Table V, entry 5) led to a decrease in yield. However, for reasons not clear, Pd(PPh$_3$)$_4$ turned out to be less effective (Table V, entry 3). Solvents like benzene, triethylamine, or THF were less efficient (data not shown) than DMF or CH$_3$CN in these coupling reactions.

The presence of a catalytic (5 mol %) or equivalent amount of copper(I) iodide changes the course of the reaction giving the normal Heck reaction coupled product, the 1,3-enyne (Table IV, entries 9 and 10), to the exclusion of the fulvene. In fact, the Pd-catalyzed coupling between an alkyne and a vinyl halide, first reported independently by Heck,[15d] Cassar,[15c] and Sonogashira,[15a] is still the method of choice to prepare stereospecifically pure 1,3-enynes.[15b] When Ag$_2$CO$_3$ was used instead of Cu(I) ion and triethylamine (Table IV, entry 11), a complicated mixture of products was obtained containing desilylated fulvene **4**. The formation of the desilylated fulvene is somewhat surprising since Ag(I) ion suppresses desilylation in the Pd-catalyzed arylation of vinylsilanes.[15e] Moreover, the absence of triethylamine rules out the possibility of desilylation by the ammonium iodide (formed from triethylamine and HI liberated during the reaction).

In order to establish the stereochemical requirement of the vinyl iodide for the Pd-catalyzed coupling, pure (*Z*)- and (*E*)-1-iodo-2-phenyl-1-ethene were synthesized. Under identical conditions (method A), the *E* isomer (Table III, entry 1) gave the expected fulvene **7** (44%), while the *Z* isomer gave a mixture of fulvenes **7** (6%), **8** (15%), and **9**[16] (6%) accompanied by unreacted starting material (8%). Treatment of 1,3-enyne **10** or 1,3-diyne **11** with excess (trimethylsilyl)acetylene (method B) for 3 days gave no sign of reaction, while (4-methoxyphenyl)acetylene and phenyl-

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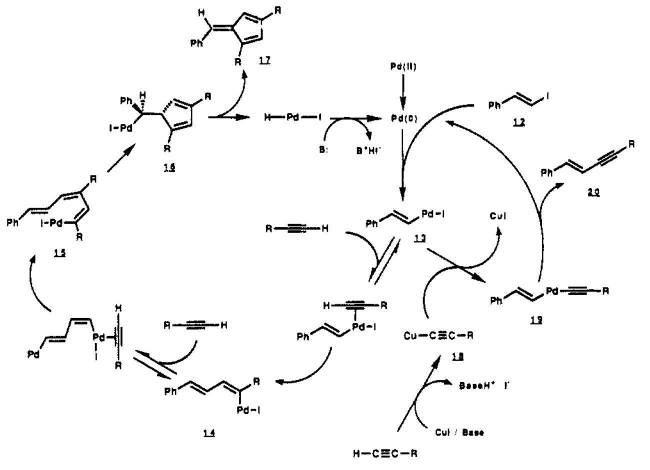
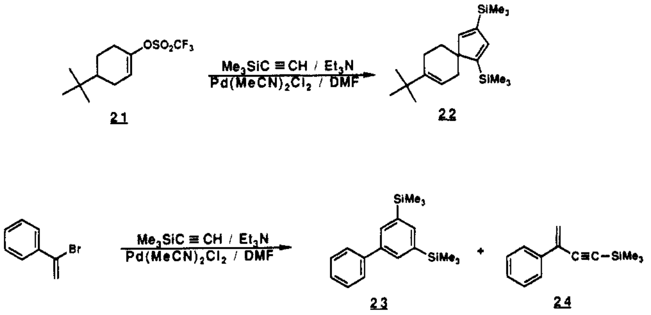
[16] Separation of **9** from **8** was unsuccessful. However, the structure of **9** was deduced from its ^{1}H NMR of which is identical with that reported in ref 7.

Scheme III. Proposed Rationalization of Fulvene and Enyne Formation



Scheme IV



acetylene (method A or B) with excess (trimethylsilyl)acetylene only led to unidentified polar products. Thus the course of Pd-catalyzed alkynylation of alkene to form the fulvene does not seem to involve intermediates such as the 1,3-enyne, 1,3-diyne, or alkyne (formed from elimination of HI from the vinyl iodide by NEt$_3$).

A possible mechanism[17] for the fulvene formation is outlined in Scheme III. Oxidative addition of Pd(0) with vinyl iodide **12** forms Pd(II) iodide (**13**). Subsequent Heck reaction between **13** and the alkyne gives vinylpalladium(II) iodide **14**. In the presence of excess alkyne, **14** is converted to triene **15**. Triene **15** undergoes a suprafacial insertion at C-5 to form **16**, which on suprafacial β-hydride elimination gives the (*E*)-fulvene **17**. In the presence of Cu(I) iodide, a different reaction course takes place. A preferable mechanism for the Cu-mediated reaction might involve Castro-formation of the copper alkyne **18**. Transmetalation of the alkyne **18** with **13** to palladium gives **19**, which on reductive elimination gives enyne **20**. The facile transmetalation between the organocopper species **18** with the organopalladium halide **13**[18] and hence **20** would explain the earlier reports[15a-d] of the exclusive formation of the 1,3-enyne in the presence of Cu(I).

Analysis of this mechanism suggests two intriguing possibilities. First, the intermolecular–intermolecular–intramolecular cascade carbopalladation of cyclic vinyl halide or equivalent should yield a [5.*n*]spiro system. To this end, exposure of 4-*tert*-butyl-1-cyclohexene triflate[19] **21** to (trimethylsilyl)acetylene and Pd(CH$_3$CN)$_2$Cl$_2$ at 25 °C, in the presence of lithium chloride, formed the [5.6]spirotriene **22** in a 49% yield (Scheme IV). Secondly, an α-substituted vinyl halide (bromide/iodide) should afford a 1-substituted-3,5-bis(silyl)benzene. Preliminary experiments show that α-bromostyrene under conditions used with the triflate or with Pd(PPh$_3$)$_2$Cl$_2$/refluxing CH$_3$CN gave 3,5-bis(trimethylsilyl)biphenyl **23** (2%), enyne **24** (2%) (Scheme IV), and unidentified polar materials. It is interesting to note that, with (trimethylsilyl)acetylene and Pd(PPh$_3$)$_2$Cl$_2$ in 100 °C in the presence or absence of copper(I) iodide, α-bromostyrene gave exclusively the corresponding enyne (Table IV, entry 2). These last reactions are being explored further.

In summary, we have developed a new and general synthesis of substituted fulvenes, based on the palladium-catalyzed [2 + 2 + 2] annulation of 1 mol of a β-substituted vinyl iodide and 2 mol of monosubstituted alkyne. In addition, the methodology can be extended to the synthesis of [6.5]spiro and biaryl systems. The details of these latter processes will be reported separately in due course.

Experimental Section

Melting points were determined in open capillary tubes on a Thomas Hoover capillary melting point apparatus and are uncorrected. UV spectra were recorded on a Beckman DU-7 spectrophotometer. ^{1}H spectra (299.943 MHz) and ^{13}C spectra (75.429 MHz) were obtained on a Varian XL-300 Advanced spectrometer using a 5-mm ^{1}H/^{13}C switchable probe. Samples were dissolved in CDCl$_3$. All spectra were obtained at 293 K. Chemical shifts are reported in δ unit (parts per million) downfield of tetramethylsilane. Splitting patterns are designated as follows: s, singlet; d, doublet; t, triplet; p, pentet; m, multiplet; and br, broad. Heteronuclear (^{1}H–^{13}C) direct and long-range connectivities were determined through HETCOR[8-10] and XCORFE[11] experiments. Spectral widths of 13 369 Hz (^{13}C) and 2690 Hz (^{1}H) were used to generate 256 × 2048 data sets that were zero filled to yield final 512 × 2048 data sets. NOE[12] difference experiments were obtained by using a 4-s selective irradiation pulse, a 1-ms delay, a 2-s acquisition time, and no relaxation delay. Low-resolution and high-resolution mass spectrum were obtained on the VG-7070E mass spectrometer. Analytical thin-layer chromatography (TLC) was performed on precoated 0.25-mm silica gel 60PF-254, and the spots were visualized with UV or by spraying with a solution of 5% phosphomolybdic acid in ethanol and heated at ca. 200 °C for a few minutes. Preparative HPLC was done on a Waters Prep LC System 500A. All reactions involving moisture-sensitive reagents were carried out in an oven or a flame-dried apparatus under argon. Tetrahydrofuran was freshly distilled from sodium benzophenone ketyl under argon before use. Unless otherwise stated, all commercial reagents including anhydrous DMF were used as received. Microanalyses were performed by the Galbraith Laboratories, Inc.

Vinyl halides **1**, **25–27** were synthesized according to Takai,[5] and their spectroscopic data are summarized as follows.

(*E*)-2-(4-Methoxyphenyl)-1-iodo-1-ethene (1): yield 50%; mp 98–9 °C; TLC (hexane) R_f 0.17; ^{1}H NMR (CDCl$_3$) 3.84 (s, 3 H), 6.66 (d, 1 H, J = 14.9 Hz), 6.87 (dd, 2 H, J = 6.8 Hz, 2.1 Hz), 7.27 (dd, 2 H, J = 6.8 Hz, 2.1 Hz), and 7.38 (d, 1 H, J = 14.9 Hz); ^{13}C NMR (CDCl$_3$) 55.2, 73.6, 113.9, 127.2, 130.5, 144.1, and 159.6; HRMS exact mass calculated for C$_9$H$_9$OI (M$^+$) 259.9698, found 259.9704.

(*E*,*Z*)-2-(2-Methylphenyl)-1-iodo-1-ethene (25): yield 63% (*E*:*Z*, 7:3); ^{1}H NMR (CDCl$_3$) *E* isomer 2.38 (s, 3 H), 6.73 (d, 1 H, J = 14.8 Hz), 7.18–7.40 (m, 4 H), and 7.68 (d, 1 H, J = 14.8 Hz); ^{13}C NMR (CDCl$_3$) 19.8, 125.7, 126.2, 128.2, 128.3, 130.4, 134.7, 136.9, and 143.3; ^{1}H NMR (CDCl$_3$) *E*,*Z* isomers 2.28 (s, 3 H), 2.36 (s, 3 H), 6.68 (d, 1 H, J = 8.4 Hz), 6.72 (d, 1 H, J = 14.8 Hz), 7.18–7.40 (m, 8 H), 7.46 (m, 1 H), and 7.68 (d, 1 H, J = 14.8 Hz); ^{13}C NMR *E*,*Z* isomers 19.7, 19.8, 125.4, 125.7, 126.2, 128.1, 128.3, 129.9, 130.3, 134.7, 135.8, 136.9, 138.9, and 143.3; LRMS *m*/*e* (% abundance) 244 (M$^+$, 100), 115 (95), and 91 (42).

(*E*)-2-(2-Naphthyl)-1-iodo-1-ethene (26): yield 57%; mp 85–6 °C, TLC (hexane) R_f 0.30; ^{1}H NMR (CDCl$_3$) 6.99 (d, 1 H, J = 15.0 Hz), 7.55 (m, 3 H), 7.62 (d, 1 H, J = 15.0 Hz), 7.73 (br s, 1 H), and 7.90 (m, 3 H); ^{13}C NMR (CDCl$_3$) 77.1, 122.7, 126.2, 126.4, 126.6, 127.7, 128.2, 128.5, 133.1, 133.3, 135.0, and 145.0; HRMS exact mass calculated for C$_{12}$H$_9$I (M$^+$) 279.9749, found 279.9749.

(*E*,*Z*)-2-(3-Thienyl)-1-iodo-1-ethene (27): ^{1}H NMR (CDCl$_3$) of *E*,*Z* isomers 6.46 (d, 1 H, J = 8.5 Hz), 6.67 (d, 1 H, J = 14.9 Hz), 7.15 (m, 2 H), 7.29 (m, 1 H), 7.41 (d, 1 H, J = 8.5 Hz), and 7.42 (d, 1 H, J = 14.9 Hz). This vinyl iodide is relatively unstable and has very similar chromatographic characteristics as that of iodoform.

(*E*)-2-Phenyl-1-iodo-1-ethene. This compound was prepared from phenylacetylene via hydroalumination and trapping with iodine similar to that reported in ref 14. The product was purified by preparative HPLC on a silica column with hexane as eluent: ^{1}H NMR (CDCl$_3$) 6.84 (d, 2 H, J = 15.0 Hz), 7.30 (m, 5 H), and 7.44 (d, 1 H, J = 15.0 Hz); ^{13}C NMR (CDCl$_3$) 76.6, 126.1, 128.5, 128.8, 137.8, and 145.2; LRMS *m*/*e* (% abundance) 230 (M$^+$, 100) 229 (19), 105 (27), 103 (80), 102 (41), 77 (51), and 51 (24).

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(17) The authors thank an anonymous referee for his valuable comments on the possible reaction mechanism.

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(*E*)-1-Iodo-1-nonene (28). This compound was prepared from 1-nonyne via hydroalumination and trapping with iodine similar to that reported in ref 14: bp 65–7 °C/1 Torr; ^{1}H NMR ($CDCl_3$) 0.91 (t, 3 H, J = 6.9 Hz), 1.29 (br s, m, 10 H), 2.05 (m, 2 H), 5.98 (dt, 1 H, J = 14.5 Hz, 1.4 Hz), 6.54 (dt, 1 H, J = 14.5 Hz, 7.2 Hz); ^{13}C NMR ($CDCl_3$) 14.1, 22.7, 28.4, 28.9, 29.1, 31.8, 36.1, 74.3, and 146.8; HRMS exact mass calculated for $C_9H_{17}I$ (M^+) 252.0375, found 252.0375.

General Procedures for the Synthesis of Fulvenes 3, 7, and 29–37 (Tables III and IV). Method A. A solution of vinyl iodide (1 equiv), triethylamine (1.2 equiv), and $Pd(CH_3CN)_2Cl_2$ (5 mol %) in dried DMF (ca. 0.1 M) was deaerated with argon, followed by addition of the alkyne (2.5 equiv). Stirring was continued at 25 °C overnight (for convenience). After most of the solvent was removed under high vacuum, the residue was diluted with a mixture of ethyl ether and water. Extraction (ethyl ether) and evaporation of the dried (magnesium sulfate) extracts gave a residue, which was purified by flash chromatography to give the desired fulvene.

Method B. A solution of vinyl iodide (1 equiv), triethylamine (1.2 equiv), and $Pd(PPh_3)_2Cl_2$ (5 mol %) in acetonitrile (ca. 0.1 M) was deaerated with argon, followed by addition of the alkyne (2.5 equiv). The mixture was refluxed until all the iodide was consumed (monitored by TLC). On cooling, the mixture was quenched with water and extracted thoroughly with ethyl ether. Evaporation of the dried (magnesium sulfate) extracts gave a residue which was purified by flash chromatography to give the desired fulvene.

6-Phenyl-1,3-bis(trimethylsilyl)fulvene (7): from (*E*)-2-phenyl-1-iodo-1-ethene, (trimethylsilyl)acetylene, and method A; TLC (hexane) R_f 0.3; ^{1}H NMR ($CDCl_3$) 0.20 (s, 9 H), 0.29 (s, 9 H), 6.85 (s, 1 H), 6.98 (s, 1 H), 7.34 (s, 1 H), 7.40 (m, 3 H), and 7.56 (d, 2 H, J = 7.3 Hz); ^{13}C NMR ($CDCl_3$) −1.17, 0.45, 128.6, 128.7, 130.8, 133.3, 137.2, 137.8, 138.2, 145.7, 149.1, and 150.8; HRMS exact mass calculated for $C_{18}H_{26}Si$ (M^+) 298.1573, found 298.1580.

6-(4-Methoxyphenyl)-1,3-bis(trimethylsilyl)fulvene (3): from (*E*)-2-(4-methoxyphenyl)-1-iodo-1-ethene, (trimethylsilyl)acetylene, and method A; TLC (5% ethyl ether/hexane) R_f 0.33; mp 93–4 °C (EtOH); ^{1}H NMR ($CDCl_3$) 0.19 (s, 9 H), 0.28 (s, 9 H), 3.85 (s, 3 H), 6.81 (s, 1 H), 6.94 (d, 2 H, J = 8.8 Hz), 6.99 (s, 1 H), 7.27 (br s, 1 H), and 7.53 (d, 2 H, J = 8.8 Hz); ^{13}C NMR ($CDCl_3$) −1.41, 0.20, 55.3, 114.4, 130.14, 132.7, 133.1, 138.2, 138.4, 145.1, 148.6, 149.3, and 160.8; UV ($CHCl_3$) λ_{max} 353 nm; HRMS exact mass calculated for $C_{19}H_{28}Si_2O$ (M^+) 328.1679, found 328.1670. Anal. Calcd for $C_{19}H_{28}Si_2O$: C, 69.49; H, 8.53. Found: C, 69.38; H, 8.77.

6-(4-Methoxyphenyl)-1,3-diphenylfulvene (29): from (*E*)-2-(4-methoxyphenyl)-1-iodo-1-ethene, phenylacetylene, and method A; TLC (5% ethyl ether/hexane) R_f 0.25; mp 110–1 °C (EtOH); ^{1}H NMR ($CDCl_3$) 3.86 (s, 3 H), 6.80–7.80 (m, 17 H); ^{13}C NMR ($CDCl_3$) 55.3, 87.2, 97.6, 114.2, 122.0, 123.5, 125.6, 126.0, 127.7, 128.3, 128.4, 128.5, 130.0, 131.5, 135.2, 135.5, 137.9, and 159.8; HRMS exact mass calculated for $C_{25}H_{20}O$ (M^+) 336.1514, found 336.1509. Anal. Calcd for $C_{25}H_{20}O$: C, 89.26; H, 5.95. Found: C, 89.13; H, 5.94.

6-(4-Methoxyphenyl)-1,3-dipropylfulvene (30): from (*E*)-2-(4-methoxyphenyl)-1-iodo-1-ethene, 1-pentyne, and method B; TLC (3% ethyl ether/hexane) R_f 0.35; ^{1}H NMR ($CDCl_3$) 1.01 (t, 3 H, J = 7.4 Hz), 1.05 (t, 3 H, J = 7.4 Hz), 1.66 (p, 4 H, J = 7.5 Hz), 2.41 (t, 2 H, J = 6.8 Hz), 2.53 (t, 2 H, J = 6.8 Hz), 3.90 (s, 3 H), 6.10 (br s, 1 H), 6.27 (br s, 1 H), 6.97 (d, 2 H, J = 8.8 Hz), 7.01 (br s, 1 H), and 7.59 (d, 2 H, J = 8.8 Hz); ^{13}C NMR ($CDCl_3$) 14.1, 14.2, 21.8, 22.6, 23.4, 28.9, 31.6, 32.6, 55.3, 113.4, 114.0, 128.1, 129.9, 130.8, 131.9, 140.2, 143.4, 150.5, and 159.1; HRMS exact mass calculated for $C_{19}H_{24}O$ (M^+) 268.1827, found 268.1814.

6-(4-Methoxyphenyl)-1,3-di-*tert*-butylfulvene (31): from (*E*)-2-(4-methoxyphenyl)-1-iodo-1-ethene, *tert*-butylacetylene, and method B; TLC (5% ethyl ether/hexane) R_f 0.47; mp 82–3 °C (EtOH); ^{1}H NMR ($CDCl_3$) 1.20 (s, 9 H), 1.39 (s, 9 H), 3.87 (s, 3 H), 6.13 (d, 1 H, J = 1.7 Hz), 6.23 (d, 1 H, J = 1.9 Hz), 6.95 (d, 2 H, J = 8.8 Hz), 7.42 (br s, 1 H), and 7.48 (d, 2 H, J = 8.8 Hz); ^{13}C NMR ($CDCl_3$) 29.4, 32.3, 32.4, 33.2, 55.2, 112.2, 114.0, 125.8, 130.1, 132.0, 134.2, 142.8, 147.9, 157.3, and 159.7; HRMS exact mass calculated for $C_{21}H_{28}O$ (M^+) 296.2140, found 296.2125. Anal. Calcd for $C_{21}H_{28}O$: C, 85.08· H, 9.45. Found: C, 85.14; H, 9.73.

6-(4-Methoxyphenyl)-1,3-bis(hydroxymethyl)fulvene (32): from (*E*)-2-(4-methoxyphenyl)-1-iodo-1-ethene, propargyl alcohol, and method A; TLC (40% ethyl acetate/hexane) R_f 0.07; ^{1}H NMR ($CDCl_3$) 2.46 (br s, 1 H), 2.66 (br s, 1 H), 3.81 (s, 3 H), 4.44 (s, 2 H), 4.55 (br s, 2 H), 6.37 (br s, 1 H), 6.52 (s, 2 H), 6.88 (d, 2 H, J = 8.8 Hz), and 7.51 (d, 2 H, J = 8.8 Hz); ^{13}C NMR ($CDCl_3$) 55.3, 58.3, 60.9, 114.4, 116.6, 128.6, 129.4, 132.7, 135.9, 139.2, 140.8, 148.0, and 160.9; HRMS exact mass calculated for $C_{15}H_{17}O_3$ $(M + 1)^+$ 245.1178, found 245.1172.

6-(2-Methylphenyl)-1,3-bis(trimethylsilyl)fulvene (33): from (*E*)-2-(2-methylphenyl)-1-iodo-1-ethene, (trimethylsilyl)acetylene, and method A: mp 74–5 °C (EtOH); ^{1}H NMR ($CDCl_3$) 0.11 (s, 9 H), 0.31 (s, 9 H), 2.39 (s, 3 H), 6.86 (br s, 1 H), 6.88 (m, 1 H), 7.27 (m, 3 H), 7.49 (s + m, 2 H); ^{13}C NMR ($CDCl_3$) −1.47, 0.12, 19.9, 126.1, 128.9, 130.3, 131.8, 134.1, 136.5, 136.8, 137.8, 137.9, 146.1, 148.9, and 151.1; HRMS exact mass calculated for $C_{19}H_{28}Si_2$ (M^+) 312.1729, found 312.1724. Anal. Calcd for $C_{19}H_{28}Si_2$: C, 73.05; H, 8.97. Found: C, 72.98; H, 9.43.

6-(2-Naphthyl)-1,3-bis(trimethylsilyl)fulvene (34): from (*E*)-2-(2-naphthyl)-1-iodo-1-ethene, (trimethylsilyl)acetylene, and method A; TLC (hexane) R_f 0.26; mp 82–3 °C (EtOH); ^{1}H NMR ($CDCl_3$) 0.23 (s, 9 H), 0.35, (s, 9 H), 6.89 (br s, 1 H), 7.08 (br s, 1 H), 7.55 (m, 3 H), 7.60 (dd, 1 H, J = 6.3 Hz, 3.4 Hz), 7.90 (m, 3 H), and 8.01 (br s, 1 H); ^{13}C NMR ($CDCL_3$) −1.45, 0.22, 126.7, 127.1, 127.8, 127.9, 128.4, 128.7, 131.3, 133.4, 133.5, 133.6, 135.0, 138.1, 138.5, 146.0, 149.5, and 151.3; HRMS exact mass calculated for $C_{22}H_{28}Si_2$ (M^+) 348.1730, found 348.1740. Anal. Calcd for $C_{22}H_{28}Si_2$: C, 75.84; H, 8.04. Found: C, 75.87; H, 8.38.

6-(3-Thienyl)-1,3-bis(trimethylsilyl)fulvene (35): from (*E*,*Z*)-2-(3-thienyl)-1-iodo-1-ethene, (trimethylsilyl)acetylene, and method A; TLC (hexane) R_f 0.40; ^{1}H NMR ($CDCl_3$) 0.21 (s, 9 H), 0.28 (s, 9 H), 6.82 (s, 1 H), 7.04 (s, 1 H), 7.27 (s, 1 H), 7.39 (br s, 2 H), and 7.50 (m, 1 H); ^{13}C NMR ($CDCl_3$) −1.4, 0.15, 126.6, 128.8, 129.1, 131.1, 132.9, 138.6, 139.3, 145.7, 148.9, and 149.8; LRMS *m*/*e* (% abundance) 304 (M^+, 14), 289 (5), 248 (14), 216 (11), 201 (12), 147 (6), and 73 (100). This fulvene is rather unstable.

6-Heptyl-1,3-bis(trimethylsilyl)fulvene (36): from (*E*)-2-heptyl-1-iodo-1-ethene, (trimethylsilyl)acetylene, and method E; ^{1}H NMR ($CDCl_3$) 0.20 (s, 9 H), 0.23 (s, 9 H), 0.89 (br t, 3 H), 1.30 (m, 8 H), 1.55 (m, 2 H), 2.58 (dt, 2 H, J = 7.1 Hz, 7.8 Hz), 6.51 (t, 1 H, J = 7.8 Hz), 6.80 (s, 1 H), and 6.90 (s, 1 H); ^{13}C NMR ($CDCl_3$) −1.43, 0.09, 13.8, 22.4, 28.9, 29.1, 29.5, 31.1, 31.6, 132.2, 137.3, 143.4, 145.4, 146.6, and 151.1; HRMS exact mass calculated for $C_{19}H_{36}Si_2$ (M^+) 320.2355, found 320.2338. About 5% of the monosilylated **37** (at C-1 or C-3) derivative was also formed (as seen from ^{1}H NMR); however, it was extremely labile and decomposed during purification.

6-(4-Methoxyphenyl)fulvene (4): from (*E*)-2-(4-methoxyphenyl)-1-iodo-1-ethene, (trimethylsilyl)acetylene, and method D; ^{1}H NMR ($CDCl_3$) 3.86 (s, 3 H), 6.33 (dt, 1 H, J = 5.0 Hz, 1.8 Hz), 6.49 (br d, 1 H, J = 5.0 Hz), 6.67 (m, 1 H), 6.72 (br d, 1 H, J = 5.2 Hz), 6.94 (dd, 2 H, J = 7.9 Hz, 2.1 Hz), 7.14 (br s, 1 H), and 7.58 (dd, 2 H, J = 7.9 Hz, 2.1 Hz); ^{13}C NMR ($CDCl_3$) 55.3, 114.3, 119.9, 127.4, 129.5, 129.8, 132.5. 134.9, 138.3, 143.3, and 160.6; HRMS exact mass calculated for $C_{13}H_{12}O$ (M^+) 184.0888, found 184.0886. The ^{1}H NMR data is identical with that reported.[7]

General Procedures for the Palladium-Catalyzed Coupling between Vinylidene Dibromide, Vinyl Halide, or Iodoalkyne and Alkynes. Synthesis of Enynes 41–47 (Table IV). Method A and Method B. These methods are the same as those described previously for the synthesis of fulvenes.

Method C. This method is similar to method A except with use of $Pd(PPh_3)_2Cl_2/Cu^II$ (5 mol % each) in Et_3N at 25 °C for 14 h (overnight).

Method D. This method is similar to method B except with use of $Pd(PPh_3)_2Cl_2$ (5 mol %)/silver carbonate (1 equiv) in CH_3CN at 100 °C for 14 h (overnight).

(4-Methylphenyl)vinylidene dibromide (38). A solution of carbon tetrabromide (10.4 g, 31 mmol) in CH_2Cl_2 (20 mL) was added to a solution of triphenylphosphine (16.0 g, 62 mmol) in CH_2Cl_2 (40 mL) at 0 °C. After 10 min, a solution of 4-methylbenzaldehyde (3.0 g, 24.9 mmol) in CH_2Cl_2 (2 mL) was added. Stirring was continued at 25 °C until all the aldehyde was consumed (4 h). The residue, after solvent removal, was purified by silica with hexane as the eluent to give 5.29 g (77%) of the titled bromide as a pale yellow oil: TLC (hexane) R_f 0.48; ^{1}H NMR ($CDCl_3$) 2.33 (s, 3 H), 7.15 (d, 2 H, J = 8.4 Hz), 7.43 (d, 2 H, J = 8.4 Hz), and 7.42 (s, 1 H); ^{13}C NMR ($CDCl_3$) 21.4, 88.5, 128.3, 129.0, 132.4, 136.7, and 138.5; LRMS *m*/*e* (% abundance) 278/276/274 (M^+, 49, 100, 51), 197/195 (12, 13), 116 (96), 115 (71), and 58 (13).

1-Iodo-5-phenyl-1-pentyne (39): *n*-Butyllithium (a 2.5 M solution in hexane, 5.89 mL, 14.7 mmol) was added to a solution of 5-phenyl-1-pentyne (2.02 g, 14.0 mmol) in THF (10 mL) at 0 °C under argon. After 1 h at 0 °C, the solution was cannulated into a solution of iodine (3.7 g, 14.7 mmol) in THF (20 mL) at −78 °C under argon. Stirring was continued overnight (15 h), while the cooling bath was allowed to attain room temperature. The mixture was diluted with ethyl ether (20 mL) and was washed successively with a saturated solution of sodium bisulfite, water, and brine. Evaporation of the dried (magnesium sulfate) organic layer gave an oil, which was purified by silica with 10% ethyl ether/hexane. Fractions with R_f of about 0.58 on evaporation gave 2.37 g (63%) of the titled iodide as a pale yellow oil: ^{1}H NMR ($CDCl_3$) 1.86 (m, 2 H), 2.40 (t, 2 H, J = 7.0 Hz), 2.73 (t, 2 H, J = 7.6 Hz), and 7.15–7.35 (m, 5 H); ^{13}C NMR ($CDCl_3$) 20.1, 29.9, 31.5, 34.5, 94.1, 125.8, 128.2, 128.3, and 141.1; LRMS (% abundance) 270 (M^+, 64%), 143 (96), 128 (100), 115 (38), and 91 (90).

1-Iodo-4-methylphenylacetylene (40). Starting from (4-methylphenyl)vinylidene dibromide (**38**) and following a literature procedure,[20] 1-iodo-(4-methylphenyl)acetylene (**40**) was obtained as a pale yellow oil (84%): TLC (hexane) R_f 0.54; ^{1}H NMR ($CDCl_3$) 2.32 (s, 3 H), 7.08 (d, 2 H, J = 8.1 Hz), and 7.30 (d, 2 H, J = 8.1 Hz); ^{13}C NMR ($CDCl_3$) 21.3, 94.3, 120.4, 128.9, 129.1, 132.3, and 139.2; HRMS exact mass calculated for C_9H_7I (M^+) 241.9593, found 241.9584.

2-(4-Methylphenyl)-1,1-bis(trimethylsilyl)-1-ethene (41): from (4-methylphenyl)vinylidene dibromide (**38**), (trimethylsilyl)acetylene, and method B; TLC (10% ethyl ether/hexane) R_f 0.67; ^{1}H ($CDCl_3$) 0.18 (s, 9 H), 0.21, (s, 9 H), 2.31 (s, 3 H), 7.00 (s, 1 H), 7.09 (d, 2 H, J = 8.0 Hz), and 7.73 (d, 2 H, J = 7.8 Hz); HRMS exact mass calculated for $C_{19}H_{26}Si_2$ (M^+) 310.1573, found 310.1566.

2-Phenyl-2-(trimethylsilyl)-1-ethene (24): from 2-bromo-2-phenyl-1-ethene, (trimethylsilyl)acetylene, and method B or method C; TLC (hexane) R_f 0.40; ^{1}H NMR ($CDCl_3$) 0.25 (s, 9 H), 5.71 (br s, 1 H), 5.93 (br s, 1 H), 7.35 (m, 3 H), and 7.65 (m, 2 H); HRMS exact mass calculated for $C_{13}H_{16}Si$ (M^+) 200.1021, found 200.1021.

7-Phenyl-1-(trimethylsilyl)-1,3-heptadiyne (42): from 1-iodo-5-phenyl-1-pentyne, (trimethylsilyl)acetylene, and method C; TLC (5% ethyl ether/hexane) R_f 0.69; ^{1}H NMR ($CDCl_3$) 0.20 (s, 9 H), 1.85 (p, 2 H, J = 7.0 Hz), 2.29 (t, 2 H, J = 7.0 Hz), 2.73 (t, 2 H, J = 7.3 Hz), and 7.15–7.30 (m, 5 H).

4-(4-Methylphenyl)-1-(trimethylsilyl)-1,3-butadiyne (43): from (4-methylphenyl)-1-iodoacetylene (**40**), (trimethylsilyl)acetylene, and method C; TLC (hexane) R_f 0.65; ^{1}H NMR ($CDCl_3$) 0.25 (s, 9 H), 2.38 (s, 3 H), 7.14 (d, 2 H, J = 8.1 Hz), and 7.41 (d, 2 H, J = 8.1 Hz); ^{13}C NMR ($CDCl_3$) −0.41, 21.6, 73.6, 88.0, 90.1, 118.2, 129.2, 132.5, and 139.7; HRMS exact mass calculated for $C_{14}H_{16}Si$ (M^+) 212.1021, found 212.1022. Also isolated from the reaction mixture was 1,4-bis(4-methylphenyl)-1,3-butadiyne (**44**, 35%): TLC (hexane) R_f 0.57; ^{1}H NMR ($CDCl_3$) 2.38 (s, 6 H), 7.15 (d, 4 H, J = 7.8 Hz), and 7.43 (d, 4 H, J = 7.8 Hz); ^{13}C NMR ($CDCl_3$) 21.6, 73.4, 81.5, 118.7, 129.2, 132.4, and 139.5; HRMS exact mass calculated for $C_{18}H_{14}$ (M^+) 230.1095, found 230.1102. When the reaction was completed by using method B, a very complicated mixture was formed, among which **44** (24%) was identified.

1-Ethoxy-4-(4-methoxyphenyl)-3-buten-1-yne (45). This compound was formed from (*E*)-2-(4-methoxyphenyl)-1-iodo-1-ethene, 1-ethoxyacetylene, and method A. The product decomposed during purification: TLC (10% ethyl ether/hexane) R_f 0.47; ^{1}H NMR ($CDCl_3$) of the crude product 1.20 (t, 3 H, J = 6.8 Hz), 3.80 (s, 3 H), 4.10 (q, 2 H, J = 6.8 Hz), 6.38 (d, 1 H, J = 15.0 Hz), 6.75 (d, 1 H, J = 15.0 Hz), 6.85 (d, 2 H, J = 8.8 Hz), and 7.35 (d, 2 H, J = 8.8 Hz).

4-(4-Methoxyphenyl)-1-(trimethylsilyl)-3-buten-1-yne (10): from (*E*)-2-(4-methoxyphenyl)-1-iodo-1-ethene, bis(trimethylsilyl)acetylene and method A or (*E*)-2-(4-methoxyphenyl)-1-iodo-1-ethene, (trimethylsilyl)acetylene, and method C; TLC (5% ethyl ether/hexane) R_f 0.46; ^{1}H NMR ($CDCl_3$) 0.24 (s, 9 H), 3.84 (s, 3 H), 6.06 (d, 1 H, J = 16.4 Hz), 6.87 (d, 2 H, J = 8.7 Hz), 7.00 (d, 1 H, J = 16.4 Hz), and 7.34 (d, 2 H, J = 8.7 Hz); ^{13}C NMR ($CDCl_3$) −0.92, −0.37, 54.9, 85.6, 88.2, 95.7, 104.9, 105.6, 114.2, 127.7, 127.9, 129.0, 142.0, and 160.4; HRMS exact mass calculated for $C_{14}H_{18}OSi$ (M^+) 230.1127, found 230.1133.

4-(4-Methoxyphenyl)-1-(tributylstannyl)-3-buten-1-yne (46): from (*E*)-2-(4-methoxyphenyl)-1-iodo-1-ethene, bis(tributylstannyl)acetylene, and method B; TLC (5% ethyl ether/hexane) R_f 0.08; ^{1}H NMR ($CDCl_3$) 0.90 (m, 9 H), 1.35 (m, 12 H), 1.60 (m, 6 H), 3.84 (s, 3 H), 6.20 (d, 1 H, J = 15.4 Hz), 6.87 (d, 2 H, J = 8.7 Hz), 6.90 (d, 1 H, J = 15.4 Hz), and 7.37 (d, 2 H, J = 8.7 Hz). The product was relatively unstable.

5-(4-Methoxyphenyl)-4-penten-2-yn-1-ol (47): from (*E*)-2-(4-methoxyphenyl)-1-iodo-1-ethene, propargyl alcohol, and method C; TLC (30% ethyl ether/hexane) R_f 0.17; ^{1}H NMR ($CDCl_3$) 1.68 (t, 1 H, J = 6.1 Hz), 3.86 (s, 3 H), 4.48 (dd, 2 H, J = 6.1 Hz, 2.1 Hz), 6.08 (dt, 1 H, J = 16.1 Hz, 2.1 Hz), 6.90 (d, 2 H, J = 8.8 Hz), 6.95 (d, 1 H, J = 16.1 Hz), and 7.36 (d, 2 H, J = 8.8 Hz); HRMS exact mass calculated for $C_{12}H_{12}O_2$ (M^+) 188.0837, found 188.0843.

Reaction between 6-(4-Methoxyphenyl)-1,3-bis(trimethylsilyl)fulvene (3) and 4-Toluenesulfinic acid. A mixture of 6-(4-methoxyphenyl)-1,3-bis(trimethylsilyl)fulvene (**3**) (119 mg, 0.36 mmol) and 4-toluenesulfinic acid[6] in acetonitrile (10 mL) containing 2% water was refluxed under argon for 3 h. On cooling, the mixture was washed with 5% $NaHCO_3$ and water and dried ($MgSO_4$). Evaporation of the extracts gave an orange oil, which was shown by ^{1}H NMR to be a mixture of desilylated fulvene **4** and monosilylated fulvene **5** in a ratio of about 1:1. Longer reaction time led to complete conversion of **5** to **4**. Unfortunately, **4** also decomposed to an appreciable amount under such conditions. Separation between **4** and **5** was achieved by preparative TLC (SiO_2; developed with 3% ethyl ether/hexane). **4** thus obtained was identical with an authentic sample obtained previously. **5**: ^{1}H NMR ($CDCl_3$) 0.21 (s, 9 H), 3.86 (s, 3 H), 6.52 (t, 1 H, J = 1.8 Hz), 6.77 (q, 2 H, J = 5.0 Hz, 1.6 Hz), 6.94 (dd, 2 H, J = 6.8 Hz, 2.0 Hz), 7.16 (br s, 1 H), and 7.60 (dd, 2 H, J = 6.8 Hz, 2.0 Hz); ^{13}C NMR ($CDCl_3$) −1.19, 55.4, 114.3, 120.2, 129.7, 132.5, 136.3, 137.9, 138.8, 143.3, 144.8, and 160.7; HRMS exact mass calculated for $C_{16}H_{20}SiO$ (M^+) 256.1283, found 256.1277.

Alternative Synthesis of 6-(4-Methoxyphenyl)fulvene (4). A solution of 4-methoxybenzaldehyde (0.45 mL, 3.69 mmol) in THF (2 mL) was added to a solution of lithium cyclopentadiene (293 mg, 4.07 mmol) in THF (20 mL) at 0 °C under argon. After 1 h, methanesulfonyl chloride (0.29 mL, 3.69 mmol), followed by triethylamine (0.52 mL, 3.69 mmol), was added. Stirring was continued for another hour at 0 °C before it was quenched with water. Extraction (ethyl ether) and evaporation of the dried ($MgSO_4$) extracts gave a residue, which was purified by flash chromatography on silica using 3% ethyl ether/hexane to give 65.1 mg (10%) of **4**, having spectroscopic data identical with an authentic sample obtained previously.

Hydrogenation of 6-(4-methoxyphenyl)-1,3-bis(trimethylsilyl)fulvene. A mixture of 6-(4-methoxyphenyl)-1,3-bis(trimethylsilyl)fulvene (**3**) (58.0 mg, 0.18 mmol) and 10% palladium/carbon (10 mg) in ethyl acetate (7 mL) was hydrogenated under atmospheric pressure at 25 °C for 12 h. The mixture was filtered through Celite, and the filtrate was evaporated down to give an oil. Purification by flash chromatography on silica using hexane gave 47.2 mg (80%) of 1-(4-methoxybenzyl)-2,4-bis(trimethylsilyl)cyclopentane (**6**) as a colorless oil: ^{1}H NMR ($CDCl_3$) −0.06 (s, 9 H), 0.07 (s, 9 H), 0.80–1.30 (m, 4 H), 1.65 (m, 1 H), 1.75 (m, 1 H), 2.10 (t, 1 H, J = 12.9 Hz), 2.50 (m, 1 H), 2.85 (dd, 1 H, J = 13.0 Hz, 2.7 Hz), 3.78 (s, 3 H), 6.81 (dd, 2 H, J = 6.7 Hz, 2.1 Hz), and 7.06 (dd, 2 H, J = 6.7 Hz, 2.1 Hz); ^{13}C NMR ($CDCl_3$) −3.0, −1.1, 28.2, 29.9, 33.5, 34.8, 39.8, 44.3, 55.1, 113.7, 129.9, 134.5 and 157.9; HRMS exact mass calculated for $C_{19}H_{34}Si_2O$ (M^+) 334.2148, found 334.2153.

(*Z*)-1-Iodo-2-phenyl-1-ethene. (a) 1-Iodo-2-phenylacetylene. *n*-Butyllithium (a 2.5 M solution in hexane, 16.4 mL, 41.1 mmol) was added dropwise to a solution of phenylacetylene (4.3 mL, 39.2 mmol) in THF at 0 °C under argon. After 30 min, a solution of iodine (10.9 g, 43.1 mmol) in THF (30 mL) was added, and stirring was continued at 25 °C overnight. The mixture was quenched with aqueous sodium bisulfite, and the layers were separated. Evaporation of the dried ($MgSO_4$) organic phase gave an oil, which was purified by flash chromatography on silica using hexane to give 5.51 g (62%) of 1-iodo-2-phenylacetylene: ^{1}H NMR ($CDCl_3$) 7.25 (m, 3 H) and 7.40 (m, 2 H). **(b) (*Z*)-1-Iodo-2-phenyl-1-ethene**: Reduction of 1-iodo-2-phenylacetylene using dipotassium azodicarbonamide[21] gave (*Z*)-1-iodo-2-phenyl-1-ethene (37%), which was purified by preparative HPLC on a silica column using hexane as eluent: ^{1}H NMR ($CDCl_3$) 6.57 (d, 1 H, J = 8.6 Hz), 7.39 (m, 5 H), 7.64 (d, 1 H, J = 8.6 Hz); ^{13}C NMR ($CDCl_3$) 79.3, 128.3, 128.5, 128.6, 136.9, and 138.8; LRMS *m/e* (% abundance) 230 (M^+, 100), 229 (26), 127 (18), 103 (99), 102 (37), 77 (46), and 76 (13).

Coupling between (*Z*)-1-Iodo-2-phenyl-1-ethene and (Trimethylsilyl)acetylene Using Method A. A mixture of (*Z*)-1-iodo-2-phenyl-1-ethene (454 mg, 1.97 mmol), (trimethylsilyl)acetylene (0.69 mL, 4.92 mmol), and triethylamine (0.33 mL, 2.36 mmol) was allowed to react by using method A. On workup and purification, the four following compounds were identified: 6-phenyl-1,3-bis(trimethylsilyl)fulvene (**7**) (6%), 6-phenyl-3-(trimethylsilyl)fulvene (**8**), (15%), 6-phenylfulvene (**9**) (6%), and unreacted (*Z*)-1-iodo-2-phenyl-1-ethene (8%). Separation of **9** from **8** was unsuccessful. However, the structure of **9** was deduced from its ^{1}H NMR of which is identical with that reported in ref 7.

6-Phenyl-1,3-bis(trimethylsilyl)fulvene (7): ^{1}H NMR ($CDCl_3$) 0.04 (s, 9 H), 0.24 (s, 9 H), 6.89 (br s, 1 H), 7.02 (br s, 1 H), 7.30 (br s, 1 H), 7.35 (m, 3 H), and 7.60 (m, 2 H); HRMS exact mass calculated for $C_{18}H_{26}Si_2$ (M^+) 298.1573, found 298.1580.

6-Phenyl-3-(trimethylsilyl)fulvene (8): ^{1}H NMR ($CDCl_3$) 0.21 (s, 9 H), 6.53 (t, 1 H, J = 1.8 Hz), 6.76 (t, 1 H, J = 1.8 Hz), 7.20 (br s, 1 H), 7.40 (m, 3 H), and 7.59 (m, 2 H).

4-(4-Methoxyphenyl)-1-(trimethylsilyl)-1,3-butadiyne (11). (a) (4-Methoxyphenyl)vinylidene dibromide. Starting from 4-methoxybenzaldehyde and using a similar procedure as for (4-methylphenyl)vinylidene dibromide (**38**) resulted in the following data: TLC (5% ethyl ether/hexane) R_f 0.20; ^{1}H NMR ($CDCl_3$) 3.82 (s, 3 H), 6.91 (d, 2 H, J = 8.8 Hz), 7.41 (s, 1 H), and 7.51 (d, 2 H, J = 8.8 Hz); LRMS *m/e* (% abundance) 294/292/290 (M^+, 49, 100, 51), 279/277/275 (10, 20, 10), 249 (6), 211 (5), 168 (8), 132 (66), 117 (22), 89 (50), and 62 (14). **(b) (4-Methoxyphenyl)acetylene.** Starting from 4-(4-methoxyphenyl)vinylidene dibromide and using a literature procedure,[20] (4-methoxyphenyl)acetylene was obtained (73%): TLC (hexane) R_f 0.14; ^{1}H NMR ($CDCl_3$) 3.00 (s, 1 H), 3.82 (s, 3 H), 6.85 (d, 2 H, J = 8.9 Hz), and 7.43 (d, 2 H, J = 8.9 Hz); LRMS *m/e* (% abundance) 132 (M^+, 100), 131

(5), 121 (47), 91 (17), 89 (60), 63 (27), and 62 (12). **(c) 4-(4-Methoxyphenyl)-1-(trimethylsilyl)-1,3-butadiyne (11).** (4-Methoxyphenyl)acetylene was coupled to (trimethylsilyl)acetylene by using method A to give **11**: TLC (3% ethyl ether/hexane) 0.33; ^{1}H NMR ($CDCl_3$) 0.21 (s, 9 H), 3.80 (s, 3 H), 6.81 (d, 2 H, J = 9.0 Hz), and 7.41 (d, 2 H, J = 9.0 Hz); HRMS exact mass calculated for $C_{14}H_{16}SiO$ (M^+) 228.0970, found 228.0978.

8-*tert*-Butyl-1,3-bis(trimethylsilyl)spiro[6.5]deca-1,3,7-triene (22): from 4-*tert*-butyl-1-cyclohexene triflate (**19**), (trimethylsilyl)acetylene, and method A with LiCl (3 equiv) gave **22** in 49% yield; ^{1}H NMR ($CDCl_3$) 0.15 (s, 18 H), 0.90 (s, 9 H), 1.35 (m, 2 H), 1.95 (m, 1 H), 2.35 (m, 1 H), 2.50–2.90 (m, 2 H), 6.25 (s, 1 H), 6.30 (br s, 1 H), and 6.70 (m, 1 H); ^{13}C NMR ($CDCl_3$) −1.50, 27.1, 28.1, 29.5, 33.2, 33.6, 49.7, 132.9, 134.2, 136.8, 142.8, 142.9, and 147.6; HRMS exact mass calculated for $C_{20}H_{37}Si_2$ (MH^+) 333.2434, found 333.2424.

3,5-Bis(trimethylsilyl)biphenyl (23) and 3-Phenyl-1-(trimethylsilyl)but-3-en-1-yne (24): from α-bromostyrene, (trimethylsilyl)acetylene, and method B gave **23** (2%) and **24** (2%); **23**, ^{1}H NMR ($CDCl_3$) 0.31 (s, 18 H), 7.35 (t, 1 H, J = 7.3 Hz), 7.45 (t, 2 H, J = 7.3 Hz), 7.59 (d, 2 H, J = 7.1 Hz), 7.66 (s, 1 H), and 7.69 (s, 2 H); ^{13}C NMR ($CDCl_3$) −1.3, 29.5, 77.2, 127.3, 127.6, 128.9, 133.1, 137.3, 140.0, 140.2, and 142.3; HRMS exact mass calculated for $C_{18}H_{26}Si_2$ (M^+) 298.1573, found 298.1572. **24**, ^{1}H NMR ($CDCl_3$) 0.25 (s, 9 H), 5.71 (br s, 1 H), 5.93 (br s, 1 H), 7.35 (m, 3 H), and 7.65 (m, 2 H); HRMS exact mass calcaulated for $C_{13}H_{16}Si$ 200.1021, found 200.1021.

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Single-Electron Transfer in Deacylation of Ethyl Dinitrobenzoates

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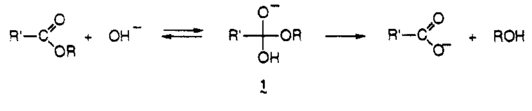
Abstract: Reactions of OH^- with ethyl 2,4- and 3,5-dinitrobenzoate (2,4-DNB and 3,5-DNB) in $DMSO/H_2O$ 1:1 (v/v) involve single-electron transfer from OH^- into the antibonding orbital of the substrate to form a charge transfer complex of $\dot{O}H$ and the radical anion. This complex collapses into a tetrahedral intermediate that gives products. Nonproductive Meisenheimer complexes form and gradually disappear. The rate and equilibrium constants of the various reaction steps can be calculated by using relaxation theory. The charge transfer complexes lead to hydrogen exchange of both substrates and products in DMSO-d_6/D_2O/OD^- and ^{1}H signals of the esters broaden during reaction. Exchange of the carboxylate ions is slow. The 2- and 4-Meisenheimer complexes of OD^- and 3,5-DNB are detected by ^{1}H NMR spectroscopy. Semiempirical MO calculations with AM1 parameters predict that formation of charge transfer and Meisenheimer complexes, and of the tetrahedral intermediate, is enthalpically favored in the absence of solvent interactions and hydration of OH^- is a significant barrier to reaction.

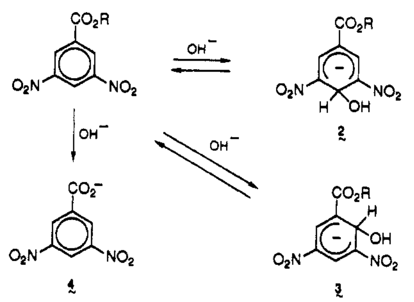
Nucleophilic attack on carboxylic esters at the acyl center in aqueous or polar media is generally assumed to generate a tetrahedral intermediate (**1**) that may partition between return to reactants and formation of products. The initial addition is written as a single step, as shown for reaction of OH^- (Scheme I).[2]

This scheme explains many features of the reactions, including structural effects and the second-order kinetic form in dilute OH^-, and there is extensive evidence for partitioning of tetrahedral intermediates.[2] This general scheme has been applied to a variety of acyl transfers. There is evidence for concerted bond making and breaking, based largely on linear free energy relations (LFER), that relate free energy of activation to basicities of entering and leaving groups.[3] Nucleophilicity is often correlated with basicity, and rates of deacylation follow basicities of nucleophiles that have a common reactive center. However, Ritchie[4] has concluded that nucleophilicity in deacylation follows N_+ values, provided that partitioning of tetrahedral intermediates is taken into account, and N_+ values correlate with oxidation potentials of the nucleophiles.[4d] Buncel, Shaik, and co-workers[5] showed that activation free energies for a variety of acyl transfers correlate with vertical ionization potentials of nucleophiles. These observations cast doubt on the general validity of LFER based on basicities but agree with descriptions of nucleophilic reactions as involving single electron transfer from nucleophile to electrophile.[6]

Scheme I



Scheme II



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