Novel Classes of Alkynyliodonium Salts and Their Applications: The Synthesis of Substituted 1,3-Diynyliodonium Triflates, R—C≡C—C≡C—I⁺—Ph ⁻OTf, and Their Reaction with Triphenylphosphine

Peter J. Stang,* Jörg Ullmann

Department of Chemistry, The University of Utah, Salt Lake City, UT 84112, USA

Dedicated to Professor Hans Bestmann upon his completion of term of office as Synthesis Executive Editor

Reaction of butadiynyltrialkyltins 1 with cyano(phenyl)iodonium triflates 2 yields 1,3-diynyl(phenyl)iodonium triflates 3, a hitherto unknown class of functionalized diacetylenes. Additionally, the reaction of 3 with triphenylphosphine is described.

In recent years there has been an increasing interest in alkynyliodonium salts that have proven to be useful precursors to novel functionalized acetylenes. The versatility of alkynyliodonium salts was best illustrated by the synthesis of various alkynyl esters[1] and -phosphonium salts.[2] Moreover, they effect many useful and unique transformations, like annulation with cyclopentene,[3] coupling with vinylcopper reagents[4] and alkynylation of organometallic complexes.[5] Several special applications have also been reported.[6]

Likewise, conjugated diynes possess interesting and versatile chemistry.[7] They are found in a number of natural products[8] and are potential phototoxic agents.[9] Therefore, the transfer of the iodonium functionality to 1,3-diynes is particularly attractive. The resulting hitherto unknown dialkynyliodonium salts 3 should have many applications similar to those of the alkynyliodonium salts. Because the access to functionalized diacetylenes is often limited,[10] a new synthetic approach is highly desirable. The high reactivity and instability of 1,3-diynes, however, often require gentle synthetic methods and considerable experimental precautions. Since the title compounds 3 are expected to have a limited stability as well, a mild and clean iodonium transfer reagent was needed for their synthesis. Based on our experience in related cases,[2] we employed cyano(phenyl)iodonium triflate (2) for this purpose, a recently developed iodinane with excellent synthetic efficiency.[2,11]

Hence, herein we wish to report our results in developing a convenient procedure for the preparation of dialkynyliodonium triflates 3 and an example of their reactivity. The synthesis of the title compounds 3 commences from readily available butadiynyltrialkyltins 1. Compounds 1 were stirred with cyano(phenyl)iodonium triflate (2) in dichloromethane at −40°C for 15 minutes yielding iodonium salts 3 in 72 to 96% isolated yield. The stability of 3 strongly depends on the alkyl substituent. Derivatives with bulky alkyl substituents (R = trimethylsilyl, *tert*-butyl) can be isolated without any special precautions. Refrigerated, the pure microcrystalline colorless salts 3a or 3b, respectively, are stable for two days. A similar stability is observed for pentadiynyl(phenyl)iodonium triflate (3c). In the case of 3d and 3e, respectively, the white powders decompose spontaneously at −20°C. However, under constant cooling and careful exclusion of air their isolation is possible as well.

All iodonium salts 3 have been fully characterized, their spectra show the combined features of diacetylenes and iodonium salts. The ^{1}H-NMR spectra of 3a–e display aromatic resonances between $\delta = 7.53$ and 8.05 in pattern and intensities typical for phenyliodonium salts. The polar nature of 3a–e is confirmed by their ^{13}C-NMR spectra by the strongly shielded position of the α-acetylenic carbon. The close and varying position of the other three acetylenic carbon signals do not allow the remaining assignment to the β, γ, and δ carbons. The IR spectra of 3a–e reveal two intense alkynyl vibrations between 2080 and 2244 cm⁻¹. All spectroscopic data are summarized in the Table.
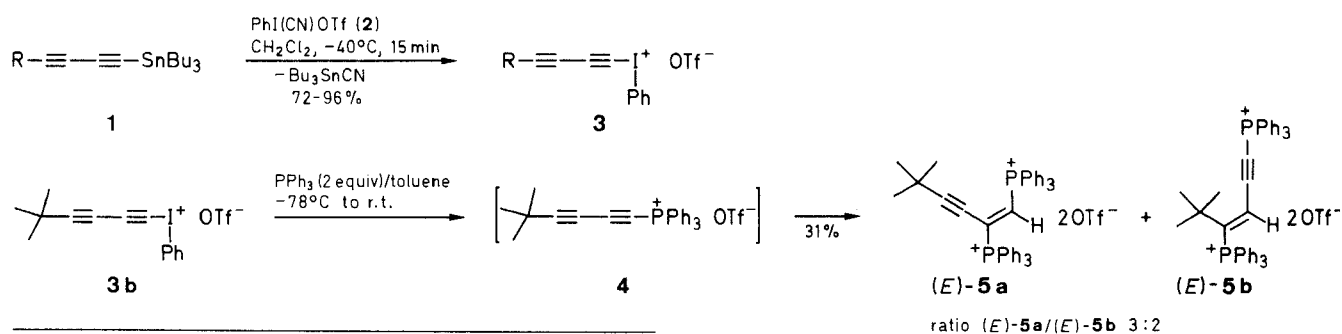
1, 3	a	b	c	d	e
R	Me₃Si	*t*-Bu	Me	Bu	Ph

Table. Physical and Spectral Properties of Compounds **1, 3** and **5**

Prod-uct	Yield (%)	Molecular Formula[a]	IR[b] v (cm^{-1})	^{1}H-NMR[c] (300 MHz) δ, J (Hz)	^{13}C-NMR[c, d] (75 MHz) δ, J (Hz)
1a	24	$C_{19}H_{36}SiSn$ (411.3)	2959, 2922, 2873, 2854, 2192, 2051, 1464, 1377, 1251, 1075, 847, 760	0.16 (s, 9H, CH$_3$Si), 0.88 (t, 9H, $J = 7.2$, CH$_3$), 0.97–1.02, 1.24–1.36, 1.48–1.59 (3m, 18H, CH$_2$)	−0.3 (s, CH$_3$Si), 11.4 ($J_{C–Sn} = 370$), 13.6, 27.0 ($J_{C–Sn} = 60$), 28.8 ($J_{C–Sn} = 23$) [4s, Bu$_3$Sn], 81.8, 87.8 ($J_{C–Sn} = 262$), 88.6 ($J_{C–Sn} = 16$), 92.3 ($J_{C–Sn} = 54$) [4s, C≡]
1b	38	$C_{20}H_{36}Sn$ (395.2)	2960, 2930, 2872, 2854, 2229, 2082, 1464, 1458, 1377, 1362, 1267, 1079, 876, 866	0.87 (t, 9H, $J = 7.3$, CH$_3$), 0.95–1.00 (m, 6H, CH$_2$), 1.21 [s, 9H, (CH$_3$)$_3$C], 1.24–1.36, 1.47–1.58 (2m, 12H, CH$_2$)	11.1 ($J_{C–Sn} = 372$), 13.5, 26.9 ($J_{C–Sn} = 60$), 28.7 ($J_{C–Sn} = 23$) [4s, Bu$_3$Sn], 27.7 [s, C(CH$_3$)$_3$], 30.4 (s, CH$_3$), 64.7 ($J_{C–Sn} = 18$), 83.2, 84.2 ($J_{C–Sn} = 308$), 92.6 ($J_{C–Sn} = 64$) [4s, C≡]
1c	73	$C_{17}H_{30}Sn$ (353.1)	2957, 2921, 2872, 2853, 2227, 2089, 1464, 1377, 1177, 1074, 876, 866, 746	0.87 (t, 9H, $J = 7.1$, CH$_3$), 0.92–1.00, 1.24–1.36, 1.48–1.58 (3m, 18H, CH$_2$), 1.88 (s, 3H, CH$_3$C≡)	4.0 (s, CH$_3$C≡), 11.2 ($J_{C–Sn} = 369$), 13.6, 26.9 ($J_{C–Sn} = 60$), 28.8 ($J_{C–Sn} = 23$) [4s, Bu$_3$Sn], 65.3 ($J_{C–Sn} = 14$), 71.6, 82.7 ($J_{C–Sn} = 285$), 92.8 ($J_{C–Sn} = 58$) [4s, C≡]
1d	53	$C_{20}H_{36}Sn$ (395.2)	2958, 2931, 2872, 2855, 2222, 2087, 1464, 1377, 1168, 1074, 876, 866, 769	0.87 (t, 12H, $J = 7.0$, CH$_3$), 0.95–1.06, 1.24–1.62 (2m, 22H, CH$_2$), 2.23 (t, 2H, $J = 6.8$, CH$_2$)	11.0 ($J_{C–Sn} = 370$), 13.3, 26.8 ($J_{C–Sn} = 59$), 28.6 ($J_{C–Sn} = 23$) [4s, Bu$_3$Sn], 13.3, 18.6, 21.7, 30.2 (4s, BuC≡), 65.9 ($J_{C–Sn} = 14$), 75.7, 82.7 ($J_{C–Sn} = 299$), 92.6 ($J_{C–Sn} = 65$) [4s, C≡]
1e[e]	80	$C_{22}H_{32}Sn$ (415.2)	–	–	–
3a	96	$C_{14}H_{14}F_3IO_3SSi$ (474.3)	3095, 2964, 2220, 2080, 1562, 1470, 1448, 1282, 1230, 1217, 1175, 1166, 1023, 848	0.16 (s, 9H, CH$_3$), 7.55 (t, 2H, $J = 7.9$, H$_{meta}$), 7.70 (t, 1H, $J = 7.5$, H$_{para}$), 8.08 (d, 2H, $J = 7.8$, H$_{ortho}$)	−1.2 (s, CH$_3$), 22.3, 85.3, 89.1, 94.2 (4s, C≡), 116.3 (s, C$_{arom}$), 119.3 (q, $J_{C–F} = 318$, CF$_3$), 132.4, 133.0, 134.6 (3s, CH$_{arom}$)
3b	84	$C_{15}H_{14}F_3IO_3S$ (458.2)	3085, 3063, 2974, 2954, 2930, 2868, 2244, 2203, 2113, 1560, 1472, 1458, 1446, 1290, 1231, 1217, 1171, 1022, 737	1.18 (s, 9H, CH$_3$), 7.53 (t, 2H, $J = 7.8$, H$_{meta}$), 7.68 (t, 1H, $J = 7.3$, H$_{para}$), 8.06 (d, 2H, $J = 8.3$, H$_{ortho}$)	20.1 (s, IC≡), 28.1 [s, C(CH$_3$)$_3$], 29.7 (s, CH$_3$), 62.7, 90.4, 94.5 (3s, C≡), 116.6 (s, C$_{arom}$), 119.5 (q, $J_{C–F} = 318$, CF$_3$), 132.4, 132.9, 134.6 (3s, CH$_{arom}$)
3c	72	$C_{12}H_8F_3IO_3S$ (416.2)	3083, 3067, 2998, 2920, 2231, 2120, 1581, 1560, 1469, 1464, 1444, 1305, 1232, 1211, 1170, 1015, 987	2.05 (s, 3H, CH$_3$), 7.54 (t, 2H, $J = 7.8$, H$_{meta}$), 7.69 (t, 1H, $J = 7.3$, H$_{para}$), 8.05 (d, 2H, $J = 8.0$, H$_{ortho}$)	4.6 (s, CH$_3$), 18.7, 62.7, 83.9, 90.2 (4s, C≡), 116.3 (s, C$_{arom}$), 119.3 (q, $J_{C–F} = 318$, CF$_3$), 132.3, 132.8, 134.3 (3s, CH$_{arom}$)
3d	80	$C_{15}H_{14}F_3IO_3S$ (458.2)	3079, 3045, 2958, 2932, 2875, 2209, 2144, 1572, 1471, 1461, 1442, 1275, 1244, 1182, 1024, 984	0.85 (t, 3H, $J = 7.2$, CH$_3$), 1.30–1.51 (2m, 4H, CH$_2$), 2.40 (t, 2H, $J = 6.9$, CH$_2$), 7.55 (t, 2H, $J = 8.0$, H$_{meta}$), 7.75 (t, 1H, $J = 7.3$, H$_{para}$), 8.06 (d, 2H, $J = 8.2$, H$_{ortho}$)	13.5 (s, CH$_3$), 18.7 (s, IC≡), 19.1, 22.1, 29.7 (3s, CH$_2$), 63.7, 88.6, 91.4 (3s, C≡), 117.0 (s, C$_{arom}$), 119.4 (q, $J_{C–F} = 319$, CF$_3$), 132.7, 133.0, 134.4 (3s, CH$_{arom}$)
3e	80	$C_{17}H_{10}F_3IO_3S$ (478.2)	3048, 2204, 2101, 1560, 1471, 1442, 1261, 1174, 1037, 738	7.35 (t, 2H, $J = 7.4$, H$'_{meta}$), 7.45 (t, 1H, $J =$ H$'_{para}$), 7.50–7.57 (m, 4H, H$'_{ortho}$, H$_{meta}$), 7.69 (t, 1H, $J = 7.3$, H$_{para}$), 8.10 (d, 2H, $J = 7.6$, H$_{ortho}$)	26.6, 72.2, 83.0, 90.1 (4s, C≡), 117.0, 118.6 (2s, C$_{arom}$), 119.6 (q, $J = 319$, CF$_3$), 128.7, 131.1, 132.6, 133.0, 133.4, 134.5 (6s, CH$_{arom}$)
5a	31[f]	$C_{46}H_{40}F_6P_2O_6S_2$[g] (928.9)	3065, 2973, 2205, 1586, 1485, 1440, 1261, 1224, 1152, 1109, 1030, 728, 689, 636	0.62 (s, 9H, CH$_3$), 7.52 (dd, 1H, $J_{H–P} = 15.8$, $J'_{H–P} = 20.7$, =CH), 7.71–7.96 (m, 30H$_{arom}$)	28.8 (s, CH$_3$), 29.2 [s, C(CH$_3$)$_3$], 75.5 (dd, $J_{C–P} = 12.1$, $J'_{C–P} = 6.7$, C≡), 114.7 (d, $J_{C–P} = 89$, C$_{arom}$), 116.7 (d, $J_{C–P} = 91$, C$_{arom}$), 121.0 (q, $J_{C–F} = 321$, CF$_3$), 130.0 (dd, $J_{C–P} = 84$, $J'_{C–P} = 14$, CH$_{arom}$), 134.3, 135.1 (2d, $J_{C–P} = 11$, CH$_{arom}$), 136.1, 136.6 (2d, $J_{C–P} = 3$, CH$_{arom}$), 136.4 (dd, $J_{C–P} = 76$, $J'_{C–P} = 11$, =CH–P)[h]
5b	31[f]	$C_{46}H_{40}F_6P_2O_6S_2$ (928.9)	3067, 2165, 1585, 1484, 1440, 1264, 1224, 1152, 1111, 1101, 1031, 726, 689, 638	1.27 (s, 9H, CH$_3$), 7.20 (dd, 1H, $J_{H–P} = 15.2$, $J'_{H–P} = 8.4$, =CH), 7.59–8.06 (m, 30H$_{arom}$)	–[i]

[a] Satisfactory microanalysis for **1** and **5** obtained: C ± 0.24, H ± 0.07, except **1c**: C −0.85, H + 0.47. For **3a–e**, no elemental analysis were performed due to their instability.

[b] **1a–d** (film), **3a–e** and **5a,b** (powder, dispersed between NaCl plates).

[c] **1a–d** recorded in CDCl$_3$, **3a–e** and **5a, b** in CD$_2$Cl$_2$. NMR spectra for **3a–e** were taken below −20°C to avoid decomposition.

[d] For **1a–d**, the carbon-tin coupling constants of the satellites are given in brackets.

[e] Spectroscopic data of **1e** are in agreement with those reported recently.[15]

[f] Total yield of **5a** and **5b**.

[g] HRMS calc. for $C_{45}H_{40}F_3O_3P_2S^+$: 779.21255; found: 779.21344.

[h] The second acetylenic carbon could not be observed, probably on account of its very low intensity.
^{31}P-NMR (121 MHz, CD$_2$Cl$_2$): $\delta = 16.5$ (d, $^3J_{P–P} = 48.0$), 28.4 (d, $^3J_{P–P} = 48.2$).

[i] ^{31}P-NMR (121 MHz, CD$_2$Cl$_2$): $\delta = 6.9$ (s, P–C≡), 22.1 (s, P–C=).

The starting tin diacetylenes **1** are prepared from metal diacetylides[12-14] with tributyltin chloride analogous to literature procedures. We have chosen to prepare the butyl substituted tin diacetylenes rather than the known methyl substituted derivatives in order to avoid difficulties during the workup in the subsequent iodonium transfer reaction. Tributyltin cyanide formed as a byproduct can be easily removed from the iodonium triflates **3** by taking advantage of its excellent solubility in hexane. In contrast, trimethyltin cyanide is almost as insoluble in hexane as **3**.

We have also investigated the ability of **3** to undergo substitution reactions. For example, compound **3b** reacts smoothly with triphenylphosphine. However, the monophosphonium salt **4**, that is formed is highly reactive and adds excess triphenylphosphine to yield the bisphosphonium salts **5a** and **5b**. Interestingly, the addition occurs to either of the two triple bonds. The triphosphonium salt formed by possible double addition of triphenylphosphine to **4** was not observed. Since the phosphonium group substituted triple bond in **4** has the higher electron deficiency, the addition takes place preferentially there to yield **5a** as the major isomer. The assignments of the E-configuration of the double bond in **5a** and **5b** is made on the basis of their proton spectra. The coupling constant $^3J_{HP}$ in the range of about 15 Hz establishes the *cis*-relationship of the proton and phosphonium substituent in both cases.

In conclusion, we have presented a simple method for the ready preparation of 1,3-diynyl(phenyl)iodonium triflates in good to excellent yields, a novel and hitherto unknown class of functionalized diacetylenes, involving a one pot procedure using known starting materials. Additionally, it has been shown that **3** can be reacted with triphenylphosphine, hence it is likely, that other nucleophiles will react with **3** as well resulting in functionalized diacetylenes. All compounds were characterized by multinuclear NMR and IR.

[4-(Tributylstannyl)-1,3-butadiynyl]trimethylsilane (1a):

A solution of lithium 4-trimethylsilyl-1,3-butadiynide, prepared from bistrimethylsilylbutadiyne (4.0 g, 20.6 mmol) and MeLi (14.7 mL of a 1.4 M solution in Et₂O, 20.6 mmol) in THF (50 mL) under N₂,[12] is cooled to − 78°C. Tributyltin chloride (5.4 mL, 20.0 mmol), dissolved in THF (10 mL), is added slowly. The mixture is allowed to warm to r.t. and is stirred for 24 h. Most of the solvent is evaporated under reduced pressure to give a black oil that is subsequently treated with hexane under vigorous stirring. The inorganic salts precipitated are filtered off, washed with hexane twice, and the solvent of the combined solutions is evaporated again. The oil obtained is distilled in vacuo yielding a colorless to slightly yellow oil. Redistillation yields pure **1a** (2.0 g, 24%); bp 215°C/1 Torr.

(5,5-Dimethyl-1,3-hexadiynyl)tributylstannane (1b):

A solution of 5,5-dimethyl-1,3-hexadiynylmagnesium bromide, prepared by refluxing a solution of EtMgBr (19.3 mmol) and 5,5-dimethyl-1,3-hexadiyne (2.60 mL, 19.3 mmol) in Et₂O (50 mL) for 5 h under N₂, is cooled to − 78°C. Tributyltin chloride (5.05 mL, 18.6 mmol), dissolved in Et₂O (10 mL), is added slowly. The mixture is allowed to warm to r.t. and is stirred for 16 h. Water is added, the phases are separated, the aqueous layer is washed with Et₂O, and the solvent of the combined organic phase is evaporated under reduced pressure, yielding a crude oil. Distillation in vacuo yields pure **1b** (2.92 g, 38%); bp 200°C/1 Torr.

1,3-Pentadiynyltributylstannane (1c):

A solution of 1,3-pentadiynylmagnesium bromide, prepared from EtMgBr (5.0 mmol) and 1,3-pentadiyne (0.32 g, 5.0 mmol) in Et₂O (50 mL) under N₂,[13] is cooled to − 78°C. Tributyltin chloride (1.22 mL, 4.6 mmol), dissolved in Et₂O (10 mL), is added slowly. The mixture is allowed to warm to r.t. and is stirred for 16 h. Water is added, the phases are separated, the aqueous layer is washed with Et₂O, and the solvent of the combined organic phase is evaporated under reduced pressure, yielding a crude oil. Distillation in vacuo yields pure **1c** (1.29 g, 73%); bp 170°C/1 Torr.

1,3-Octadiynylitributylstannane (1d) and (4-Phenyl-1,3-butadiynyl) tributylstannane (1e):

A solution of lithium 1,3-octadiynide[14] (6.45 mmol) or lithium 4-phenyl-1,3-butadiynide[14] (6.45 mmol), respectively, in Et₂O (50 mL) under N₂ is cooled to − 78°C. Tributyltin chloride (1.74 mL, 6.40 mmol), dissolved in Et₂O (10 mL), is added slowly. The mixture is allowed to warm to r.t. and is stirred additionally for 3 h. Water is added, the phases are separated, the aqueous layer is washed with Et₂O, and the solvent of the combined organic phase is evaporated under reduced pressure, yielding a crude oil. Distillation in vacuo yields pure **1d** (1.35 g, 53%): bp 170−180°C/ 1 Torr or **1e** (2.14 g, 80%): bp 200°C/0.1 Torr, respectively.

1,3-Diynyliodonium Triflates 3; General Procedure:

Cyano(phenyl)iodonium triflate[2,11] (**2**) (1 equiv) in CH₂Cl₂ (30 mL/mmol) under N₂, is cooled to − 40°C. Tin acetylene **1** (1 equiv), dissolved in CH₂Cl₂ (5 mL/mmol), is added dropwise. After the addition is completed, the heterogeneous mixture turns into a slightly yellow solution.

Workup for **3a−c**: The mixture is allowed to warm to r.t. within 15 min. Concentration under reduced pressure yields a yellowish oil that is crystallized by adding it to vigorously stirred hexane. After the precipitate is settled, the solvent is decanted, and the white powder is washed with hexane twice. The microcrystalline solid after drying in vacuo (r.t., 1 Torr) is spectroscopically pure.

Workup for **3d, e**: After stirring for 15 min, hexane, cooled to − 40°C, is added to the cold mixture causing an immediate precipitation. After decantation of the solvent, the white powder is washed with hexane twice and is dried in vacuo (− 30°C, 1 Torr). The microcrystalline solid, however, decomposes considerably above − 20°C.

(E)-5,5-Dimethyl-1,2-bis(triphenylphosphonio)hex-1-en-3-yne Ditriflate (5a) and (E)-5,5-Dimethyl-1,4-bis(triphenylphosphonio)hex-3-en-1-yne Ditriflate (5b):

5,5-Dimethyl-1,3-hexadiynyl(phenyl)iodonium triflate (**3b**) (0.88 g, 1.75 mmol) is added to toluene (50 mL) and cooled to − 78°C under N₂. Triphenylphosphine (0.92 g, 3.50 mmol), dissolved in toluene (5 mL), is added dropwise. The mixture is stirred at − 78°C for 10 min, the cooling bath is removed allowing the dark yellow solution to warm to r.t. After stirring at r.t. for another 10 min, Et₂O is added to separate out an oil, that is washed twice with additional Et₂O. The oil is crystallized from CH₂Cl₂/Et₂O yielding white crystals that are first washed with toluene, then with Et₂O to remove unreacted triphenylphosphine. Recrystallisation gives pure **5a**. Isomer **5b** is obtained from the mother liquor by adding hexane. Double recrystallisation is necessary to remove small amounts of **5a** and other byproducts. Total yield of **5a** and **5b**: 0.5 g (31%) in a ratio of 3:2; **5a**, mp 182°C; **5b**, mp 137−140°C.

(1) Stang, P.J.; Kitamura, T.; Arif, A.M.; Karny, M.; Apeloig, Y.
     J. Am. Chem. Soc. 1990, 112, 374.
     Lodaya, J.S.; Koser, G.F. J. Org. Chem. 1990, 55, 1513.
     Stang, P.J.; Kitamura, T.; Boehshar, M.; Wingert, H. J. Am.
     Chem. Soc. 1989, 111, 2225.
     Stang, P.J.; Boehshar, M.; Wingert, H.; Kitamura, T. J. Am.
     Chem. Soc. 1988, 110, 3272.
     Stang, P.J.; Surber, B.W.; Chen, Z.C ; Roberts, K.A.;
     Anderson, A.G. J. Am. Chem. Soc. 1987, 109, 228.
     Stang, P.J.; Boehshar, M.; Lin, J. J. Am. Chem. Soc. 1986,
     108, 7832.
     Stang, P.J.; Surber, B.W. J. Am. Chem. Soc. 1985, 107, 1452.
(2) Stang, P.J.; Zhdankin, V.V. J. Am. Chem. Soc. 1990, 112,
     6437.
     Stang, P.J.; Zhdankin, V.V. J. Am. Chem. Soc. 1991, 113,
     4571.
(3) Ochiai, M.; Kunishima, M.; Nagao, Y.; Fuji, K.; Shiro, M.;
     Fujita, E. J. Am. Chem. Soc. 1986, 108, 8281.
(4) Stang, P.J.; Kitamura, T. J. Am. Chem. Soc. 1987, 109, 7561.
(5) Stang, P.J.; Crittell, C.M. Organometallics 1990, 9, 3191.
(6) Bachi, M.D.; Bar-Ner, N.; Crittell, C.M.; Stang, P.J.;
     Williamson, B.L. J. Org. Chem. 1991, 56, 3912
     Stang, P.J.; Wingert, H.; Arif, A.M. J. Am. Chem. Soc. 1987,
     109, 7235.
     Margida, A.J.; Koser, G.F. J. Org. Chem. 1984, 49, 4703.
     Carman, C.S.; Koser, G.F. J. Org. Chem. 1983, 48, 2534.

(7) For some recent examples see: Lee, T.S.; Lee, S.J.; Shim, S.C.
     J. Org. Chem. 1990, 55, 4544.
     Williams, R.A.; Hanusa, T.P.; Huffman, J.C. J. Am. Chem.
     Soc. 1990, 112, 2454.
     Miller, J.A.; Zweifel, G. J. Am. Chem. Soc. 1983, 105, 1383.
(8) Jones, E.R.H.; Thaller, V. in: Chemistry of the Carbon-Carbon
     Triple Bond, Patai, S. (ed); Wiley, New York, 1978, p.621.
(9) Hudson, J.B.; Graham, E.A.; Towers, G.H.N. Photochem.
     Photobiol. 1986, 43, 27 and previous papers in this journal.
(10) Shostakovskii, M.F. The Chemistry of Diacetylenes, Wiley,
     New York, 1974.
     Niedballa, U., in: Houben-Weyl, 4th Ed., Vol. V/2a, Thieme,
     Stuttgart, 1977, p.913.
(11) Zhdankin, V.V.; Crittell, C.M.; Stang, P.J.; Zefirov, N.S.
     Tetrahedron Lett. 1990, 31, 4828.
(12) Holmes, A.B.; Jones, G.E. Tetrahedron Lett. 1980, 21, 3111.
(13) Shakhovskoi, B.G.; Stadnickuk, M.D.; Petrov, A.A. Zh.
     Obshch. Khim. 1964, 34, 2625; C.A. 1964, 61, 16087h. The
     formation of 1,3-pentadiynylmagnesium bromide, however, is
     completed in 30 min, if the ethereal solution of 1,3-pentadiyne
     and ethylmagnesium bromide is refluxed.
(14) Himbert, G.; Umbach, H.; Barz, M. Z. Naturforsch. 1984,
     39b, 661.
(15) Rubin, Y.; Knobler, C.B.; Diederich, F. J. Am. Chem. Soc.
     1990, 112, 1607.