Novel Classes of Alkynylidonium Salts and Their Applications: The Synthesis of Substituted 1,3-Diynylidonium Triflates, $R - C\equiv C - C\equiv C - I - Ph^+ OTf^-$, and Their Reaction with Triphenylphosphine

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

Reaction of butadiynyltrialkylsils 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 alkynylidonium salts that have proven to be useful precursors to novel functionalized acetylenes. The versatility of alkynylidonium salts was best illustrated by the synthesis of various alkynyl esters and phosphonium salts. Moreover, they effect many useful and unique transformations, like annulation with cyclopentene, coupling with vinylcopper reagents and alkynylation of organometallic complexes. Several special applications have also been reported.

Likewise, conjugated diynes possess interesting and versatile chemistry. They are found in a number of natural products and are potential phototoxic agents. Therefore, the transfer of the iodonium functionality to 1,3-diynes is particularly attractive. The resulting hitherto unknown dialkynylidonium salts 3 should have many applications similar to those of the alkynylidonium salts. Because the access to functionalized diacetylenes is often limited, 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, we employed cyano(phenyl)iodonium triflate (2) for this purpose, a recently developed iodinane with excellent synthetic efficiency.

Hence, herein we wish to report our results in developing a convenient procedure for the preparation of dialkynylidonium triflates 3 and an example of their reactivity. The synthesis of the title compounds 3 commences from readily available butadiynyltrialkylsils 1. Compounds 1 were stirred with cyano(phenyl)iodonium triflate (2) in dichloromethane at $-40^\circ C$ 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 ($R = \text{trimethylsilyl, tert-butyl}$) 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 $-20^\circ C$. 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 phenylidonium salts. The polar nature of 3a–e is confirmed by their $^{13}$C-NMR spectra by the strongly shielded position of the $\alpha$-acetylenic carbon. The close and varying position of the other three acetylenic carbon signals do not allow the remaining assignment to the $\beta$, $\gamma$, and $\delta$ 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.

![Chemical structure images]

<table>
<thead>
<tr>
<th>R</th>
<th>$\text{Me}_3\text{Si}$</th>
<th>$i$-Bu</th>
<th>Me</th>
<th>Bu</th>
<th>Ph</th>
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<tbody>
<tr>
<td>1, 3</td>
<td>a</td>
<td>b</td>
<td>c</td>
<td>d</td>
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ratio $(E)$_5a/$(E)$_5b 3:2
<table>
<thead>
<tr>
<th>Product</th>
<th>Yield (%)</th>
<th>Molecular Formula</th>
<th>IR $\nu$ (cm$^{-1}$)</th>
<th>$^1$H-NMR $\delta$ (300 MHz)</th>
<th>$^{13}$C-NMR $\delta$ (75 MHz)</th>
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<tbody>
<tr>
<td>1a</td>
<td>24</td>
<td>C$<em>{19}$H$</em>{35}$SiSn</td>
<td>2929, 2292, 2873, 2854, 2192, 2051, 1463, 1377, 1251, 1075, 847, 760</td>
<td>0.16 (s, 9H, CH$_3$), 0.88 (t, 9H, J = 7.2, CH$_3$), 0.97<del>1.02, 1.24</del>1.36, 1.48~1.59 (3m, 18H, CH$_3$)</td>
<td>-0.3 (s, CH$<em>3$), 11.4 (J$</em>{C-Sn}$ = 370), 13.6, 27.0 (J$<em>{C-Sn}$ = 60), 28.8 (J$</em>{C-Sn}$ = 23) [4S, Bu$<em>3$Sn], 81.8, 87.8 (J$</em>{C-Sn}$ = 262), 88.6 (J$_{C-Sn}$ = 16) [4S, C$_2$H$_5$]</td>
</tr>
<tr>
<td>1b</td>
<td>38</td>
<td>C$<em>{20}$H$</em>{36}$Sn</td>
<td>2960, 2390, 2872, 2854, 2229, 2082, 1464, 1458, 1377, 1362, 1267, 1079, 876, 866</td>
<td>0.85 (t, 9H, J = 7.3, CH$_3$), 0.95<del>1.00 (m, 6H, CH$_2$), 1.21 (s, 9H, CH$_3$)$_3$, 1.24</del>1.36, 1.47~1.58 (2m, 12H, CH$_2$)</td>
<td>-0.3 (s, CH$<em>3$), 11.4 (J$</em>{C-Sn}$ = 370), 13.6, 27.0 (J$<em>{C-Sn}$ = 60), 28.8 (J$</em>{C-Sn}$ = 23) [4S, Bu$<em>3$Sn], 81.8, 87.8 (J$</em>{C-Sn}$ = 262), 88.6 (J$_{C-Sn}$ = 16) [4S, C$_2$H$_5$]</td>
</tr>
<tr>
<td>1c</td>
<td>73</td>
<td>C$<em>{25}$H$</em>{36}$Sn</td>
<td>2957, 2291, 2872, 2853, 2229, 2082, 1464, 1377, 1174, 1074, 876, 866, 746</td>
<td>0.80 (t, 9H, J = 7.1, CH$_3$), 0.92<del>1.00, 1.24</del>1.36, 1.48~1.60 (3m, 18H, CH$_2$), 1.88 (s, 3H, CH$_3$)$_3$</td>
<td>-0.3 (s, CH$<em>3$), 11.4 (J$</em>{C-Sn}$ = 370), 13.6, 27.0 (J$<em>{C-Sn}$ = 60), 28.8 (J$</em>{C-Sn}$ = 23) [4S, Bu$<em>3$Sn], 81.8, 87.8 (J$</em>{C-Sn}$ = 262), 88.6 (J$_{C-Sn}$ = 16) [4S, C$_2$H$_5$]</td>
</tr>
<tr>
<td>1d</td>
<td>53</td>
<td>C$<em>{25}$H$</em>{36}$Sn</td>
<td>2958, 2291, 2872, 2855, 2229, 2087, 1464, 1377, 1168, 1074, 876, 866, 769</td>
<td>0.87 (t, 12H, J = 7.0, CH$_3$), 0.95<del>1.06, 1.24</del>1.62 (2m, 22H, CH$_2$), 2.23 (t, 2H, J = 6.8, CH$_3$)</td>
<td>-0.3 (s, CH$<em>3$), 11.4 (J$</em>{C-Sn}$ = 370), 13.6, 27.0 (J$<em>{C-Sn}$ = 60), 28.8 (J$</em>{C-Sn}$ = 23) [4S, Bu$<em>3$Sn], 81.8, 87.8 (J$</em>{C-Sn}$ = 262), 88.6 (J$_{C-Sn}$ = 16) [4S, C$_2$H$_5$]</td>
</tr>
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* Satisfactory microanalysis for 1 and 5 obtained: C $\pm$ 0.24, H $\pm$ 0.07, except 1c: C $\pm$ 0.85, H $\pm$ 0.47. For 3a–e, no elemental analysis were performed due to their instability.

$^a$ 1a–d (film), 3a–e and 5a,b (powder, dispersed between NaCl plates).

$^b$ 1a–d recorded in CDCl$_3$, 3a–e and 5a,b in CD$_2$Cl$_2$. NMR spectra for 3a–e were taken below $-20^\circ$C to avoid decomposition.

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

$^c$ Spectroscopic data of 1e are in agreement with those reported recently.$^{15}$

$^d$ Total yield of 5a and 5b.

$^e$ HRMS calc. for C$_{46}$H$_{64}$F$_6$P$_2$O$_4$S$_2$: 779.21255; found: 779.21344.

$^f$ The first acetylenic carbon could not be observed, probably on account of its very low intensity.

$^{15}$ P-NMR (121 MHz, CD$_2$Cl$_2$): $\delta$ = 16.5 (d, $J_{C-P}$ = 48.0), 28.4 (d, $J_{C-P}$ = 48.2).
The starting tin diacylenes 1 are prepared from metal diacetyldienes\(^2\)\(^-\)\(^4\) with tributyltin chloride analogous to literature procedures. We have chosen to prepare the butyl substituted tin diacylenes 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, which 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 phosphonium 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 \(J_{\text{HP}}\) 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 diacylenes, 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 diacylenes. All compounds were characterized by multinuclear NMR and IR.

\[\text{[4-(Tributylstannyl)-1,3-butadiynyl]trimethylsilane (1a)}:\]
A solution of lithium 4-trimethylsilyl-1,3-butadiyne, prepared from bistrimethylsilylbutyne (4.0 g, 20.6 mmol) and MeLi (14.7 mL of a 1.4 M solution in Et\(_2\)O, 20.6 mmol) in THF (50 mL) under N\(_2\), is cooled to \(-78^\circ\)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.

\[\text{[5,5-Dimethyl-1,3-hexiadinyloctyl]tributylstannane (1b)}:\]
A solution of 5,5-dimethyl-1,3-hexiadinyloctylmagnesium bromide, prepared by refluxing a solution of Et\(_3\)MgBr (19.3 mmol) and 5,5-dimethyl-1,3-hexadiyne (2.60 mL, 19.3 mmol) in Et\(_2\)O (50 mL) for 5 h under N\(_2\), is cooled to \(-78^\circ\)C. Tributyltin chloride (5.05 mL, 18.6 mmol), dissolved in Et\(_2\)O (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 Et\(_2\)O, 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 Et\(_3\)MgBr (5.0 mmol) and 1,3-pentadiyne (0.32 g, 5.0 mmol) in Et\(_2\)O (50 mL) under N\(_2\), is cooled to \(-78^\circ\)C. Tributyltin chloride (1.22 mL, 4.6 mmol), dissolved in Et\(_2\)O (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 Et\(_2\)O, 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-Octadiynyltributylstannane (1d) and (4-Phenyl-1,3-butadiynyl) tributylstannane (1e):
A solution of lithium 1,3-octadiyne\(^1\)\(^4\) (6.45 mmol) or lithium 4-phenyl-1,3-butadiyne\(^1\)\(^4\) (6.45 mmol), respectively, in Et\(_2\)O (50 mL) under N\(_2\) is cooled to \(-78^\circ\)C. Tributyltin chloride (1.74 mL, 6.40 mmol), dissolved in Et\(_2\)O (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 Et\(_2\)O, and the soluble 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-Dinyliodionium Triflates 3: General Procedure:
Cyanophenyl)iodonium triflate\(^2\)\(^1\)\(^1\) (1 equiv) in CH\(_2\)Cl\(_2\) (30 mL/mmol) under N\(_2\), is cooled to \(-40^\circ\)C. Tin acetylene (1 equiv), dissolved in CH\(_2\)Cl\(_2\) (5 mL/mmol), is added dropwise. After the addition is completed, the heterogeneous mixture turns into a slightly yellow solution.

Workup for 3a–e: 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, however, decomposes considerably above 20°C.

(E)-5,5-Dimethyl-1,3-bis(triphenylphosphino)hex-1-en-3-ynyl Ditriflate (5a) and (E)-5,5-Dimethyl-1,4-bis(triphenylphosphino)hex-3-en-1-ynyl 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 \(-78^\circ\)C under N\(_2\). Triphenylphosphine (0.92 g, 3.50 mmol), dissolved in toluene (5 mL), is added dropwise. The mixture is stirred at \(-78^\circ\)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, Et\(_2\)O is added to separate out an oil, that is washed twice with additional Et\(_2\)O. The oil is crystallized from CH\(_2\)Cl\(_2\)/Et\(_2\)O yielding white crystals that are first washed with toluene, then with Et\(_2\)O 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.

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(5) Stang, P.J.; Critell, C.M. Organometallics 1990, 9, 3191.
(13) Shakovskoi, B.G.; Stadnicks, 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.