### Instructions for use

**Title**

Direct synthesis of alkynyl(phenyl)iodonium salts from 1-alkynes

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Direct synthesis of alkynyl(phenyl)iodonium salts from 1-alkynes

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Alkynyl(aryl)iodonium salts have been recently used as versatile reagents for organic synthesis.1 They are generally prepared from 1-alkynes in two-steps via the corresponding 1-trimethylsilyle- or 1-trialkylstannyl derivatives.2 Direct conversion of 1-alkynes to alkynyl(iodonium) salts is more efficient and desirable, and has been studied by many chemists.3 However, the direct synthetic methods, which include the reaction of 1-alkynes with hydroxy(sulfonyloxy)iodo)arenes, were applicable only for the synthesis of aryl or sterically hindered alkyl group substituted alkynyl(iodonium) salts, and in other cases, the competitive formation of alkynyl(iodonium) salts was a serious problem.3a,b Therefore, the two-step method has been the sole way for the synthesis of the alkynyl(iodonium) salts with a normal alkyl group. We wish to report here the direct synthesis of 1-alkynyl(iodonium) salts from 1-alkynes of the normal alkyl chain without the formation of the alkynyl(iodonium) salts.

To a CH2Cl2 solution of iodosobenzene were added an aqueous solution of HBF4 and a catalytic amount of HgO at room temperature, and the mixture was stirred for a few minutes until the solid part dissolved completely. To the resulting mixture, 1-dodecyn (83 mg, 0.5 mmol) was added and the mixture was stirred at room temperature until the yellow color of the aqueous phase disappeared. Then the mixture was poured into a 5% aqueous solution of NaBF4 (20 ml, 1 mmol) and the separated aqueous phase was extracted with CH2Cl2 three times. The combined organic phases were dried over MgSO4 and concentrated under reduced pressure. The product was solidified by dissolving the resulting viscous liquid in a little CH2Cl2, followed by the addition of a large quantity of hexane. The liquid part was removed by decantation, and the remained solid was washed with hexane. Finally, the solvent was removed completely under reduced pressure to give 1-dodecynyl(phenyl)iodonium tetrafluoroborate (173 mg, 0.37 mmol). Characterization data for 1-dodecynyl(phenyl)iodonium tetrafluoroborate: white solid, M.p. 52 °C; δi (400 MHz, CDCl3): 8.05 (2H, d, J = 6.7 Hz), 7.68-7.54 (3H, m), 1.64-1.56 (2H, m), 1.36-1.25 (16H, m), 0.88 (3H, t, J = 6.7 Hz); δi (100.4 MHz, CDCl3): 133.82, 132.81, 132.63, 114.47, 114.02, 31.82, 29.47, 29.34, 28.73, 27.54, 22.63, 20.83, 15.86, 14.08. v (KBr) cm⁻¹ 2170, 1057, 739: HRMS (FAB): m/z 369.1096 (M-BF4).

Table 1

<table>
<thead>
<tr>
<th>R</th>
<th>Reaction time (min)</th>
<th>Yield(%)</th>
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<tbody>
<tr>
<td>Bu</td>
<td>30</td>
<td>61</td>
</tr>
<tr>
<td>tBu</td>
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<td>86</td>
</tr>
<tr>
<td>C10H21</td>
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<td>76</td>
</tr>
<tr>
<td>Cl-(CH2)9</td>
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</tr>
<tr>
<td>tBuO-(CH2)9</td>
<td>15</td>
<td>79c</td>
</tr>
<tr>
<td>MeOOC-(CH2)9</td>
<td>15</td>
<td>78c</td>
</tr>
<tr>
<td>AcO-(CH2)9</td>
<td>60</td>
<td>54</td>
</tr>
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Notes and references


