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Author(s)	Yoshida, Masanori; Nishimura, Naoya; Hara, Shoji
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## Direct synthesis of alkynyl(phenyl)iodonium salts from 1-alkynes

Masanori Yoshida, Naoya Nishimura, and Shoji Hara\*

Division of Molecular Chemistry, Graduate School of Engineering, Hokkaido University, Sapporo 060-8628, Japan. E-mail:hara@org-mc.eng.hokudai.ac.jp

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## Alkynyliodonium salts can be directly prepared from 1alkynes by the reaction with iodosobenzene, tetrafluoroboric acid, and a catalytic amount of HgO.

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 1trimethylsilyl- or 1-trialkylstannyl derivatives. Direct conversion of 1-alkynes to alkynyliodonium salts is more efficient and desirable, and has been studied by many chemists.<sup>2</sup> 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 alkynyliodonium salts, and in other cases, the competitive formation of alkenyliodonium salts was a serious problem.<sup>3a,b,</sup> Therefore, the two-step method has been the sole way for the synthesis of the alkynyliodonium salts with a normal alkyl group. We wish to report here the direct synthesis of 1-alkynyliodonium salts from 1-alkynes of the normal alkyl chain without the formation of the alkenyliodonium salts.

To a  $CH_2Cl_2$  solution of iodosobenzene were added an aqueous solution of HBF<sub>4</sub> and a catalytic amount of HgO to give two liquid phases, a clear organic phase and a clear yellow aqueous phase. When 1-alkyne was added to the mixture, the yellow color of the aqueous phase faded, and the formation of 1-alkynyl(phenyl)iodonium salt and the absence of the 1-alkyne and the alkenyliodonium salt could be confirmed from <sup>1</sup>HNMR of the mixture. The 1-alkynyl(phenyl)iodonium salts could be isolated in good yields as BF<sub>4</sub> salts (Scheme 1).

$$R-C=CH \xrightarrow{PhIO, HBF_4} R-C=C-IPh$$

## Scheme 1.

R. Caple et al. succeeded to prepare pentynyl(phenyl)iodonium tetrafluoroborate tetrafluoroborate.<sup>4</sup> from 1-pentyne and iodosobenzene However, the synthesis of any other alkynyliodonium salts was not shown and it is a serious disadvantage of their method to use a large excess of 1-pentyne (ca. 40 times) to iodosobenzene tetrafluoroborate. According to our method, various kinds of the alkynyl(phenyl)iodonium slats can be prepared from the corresponding 1-alkynes. The alkynes having both normal alkyl group and sterically hindered one can be converted to the alkynyliodonium salts without a large excess reagents. Moreover, the introduction of functional groups such as an ester, ketone, or chloride is also possible. (Table 1). † It is drawback to use a harmful mercury slat but less than 0.5 mol% of HgO is enough to obtain the alkynyliodonium salts in good yield. It is also advantage of our method that PhIO, HBF<sub>4</sub>, and HgO are all commercially available, while iodosobenzene tetrafluoroborate is not.

## Notes and references

Typical experimental procedure: To a CH<sub>2</sub>Cl<sub>2</sub> suspension (2 ml) of iodosylbenzene (132 mg, 0.6 mmol) were added 42% aqueous solution of HBF<sub>4</sub> (7.2 ml, 3 mmol) and HgO (0.54 mg, 0.0025 mmol) at room temperature, and the mixture was stirred for a few minutes until the solid part dissolved completely. To the resulting mixture, 1-dodecyne (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 The combined organic phases were dried over MgSO4 and times. concentrated under reduced pressure. The product was solidified by dissolving the resulting viscous liquid in a little CH<sub>2</sub>Cl<sub>2</sub>, 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 1dodecynyl(phenyl)iodonium tetrafluoroborate (173 mg, 0.37 mmol). 1-dodecynyl(phenyl)iodonium Characterization data for tetrafluoroborate: white solid, M.p. 52 °C.  $\delta_{\rm H}$  (400 MHz, CDCl<sub>3</sub>): 8.05 (2H, d, J = 8.1 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).  $\delta_{\rm C}$  (100.4 MHz, CDCl<sub>3</sub>): 133.82, 132.81, 132.63, 114.47, 114.02, 31.82, 29.47, 29.34, 29.32, 28.85, 28.73, 27.54, 22.63, 20.83, 15.86, 14.08. v (KBr) cm<sup>-1</sup> 2170, 1057, 739: HRMS (FAB): m/z 369.1096 (M-BF<sub>4</sub><sup>-</sup>) calcd for C<sub>18</sub>H<sub>26</sub>I 369.1079.

Table 1 Direct synthesis of alkynyl(phenyl)iodonium salts<sup>a</sup>

R	Reaction time (min)	Yield(%) <sup>b</sup>
Bu	30	61
${}^{t}\mathrm{B}\mathfrak{u}$	40	86
$C_{10}H_{21}$	30	76
CH <sub>2</sub>	60	78
CI-(CH <sub>2</sub> ) <sub>9</sub>	30	80
<sup>t</sup> BuC(=O)-(CH <sub>2</sub> ) <sub>9</sub>	15	79 <sup>c</sup>
MeOOC-(CH <sub>2</sub> ) <sub>9</sub>	15	78°
AcO-(CH <sub>2</sub> ) <sub>9</sub>	60	54

<sup>*a*</sup> The reaction was carried out as described in the note. <sup>*b*</sup> Isolated yield based on alkyne used. <sup>*c*</sup> Isolated as liquid.

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