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

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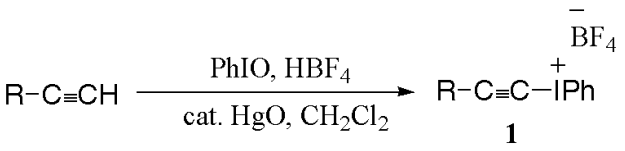
Alkynyliodonium salts can be directly prepared from 1-alkynes by the reaction with iodosobenzene, tetrafluoroboric acid, and a catalytic amount of HgO.

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 1-trimethylsilyl- or 1-trialkylstannyl derivatives.[2] Direct conversion of 1-alkynes to alkynyliodonium 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 alkynyliodonium salts, and in other cases, the competitive formation of alkenyliodonium salts was a serious problem.[3a,b,] 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_4 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 ^{1}HNMR of the mixture. The 1-alkynyl(phenyl)iodonium salts could be isolated in good yields as BF_4 salts (Scheme 1).



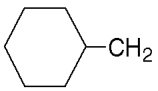
Scheme 1.

R. Caple *et al.* succeeded to prepare pentynyl(phenyl)iodonium tetrafluoroborate from 1-pentyne and iodosobenzene tetrafluoroborate.[4] 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_4, and HgO are all commercially available, while iodosobenzene tetrafluoroborate is not.

Notes and references

† Typical experimental procedure: To a CH_2Cl_2 suspension (2 ml) of iodosylbenzene (132 mg, 0.6 mmol) were added 42% aqueous solution of HBF_4 (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 $NaBF_4$ (20 ml, 1 mmol) and the separated aqueous phase was extracted with CH_2Cl_2 three times. The combined organic phases were dried over $MgSO_4$ and concentrated under reduced pressure. The product was solidified by dissolving the resulting viscous liquid in a little CH_2Cl_2, 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. δ_H (400 MHz, $CDCl_3$): 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). δ_C (100.4 MHz, $CDCl_3$): 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. ν (KBr) cm^{-1} 2170, 1057, 739: HRMS (FAB): m/z 369.1096 (M-BF_4^-) calcd for $C_{18}H_{26}I$ 369.1079.

Table 1 Direct synthesis of alkynyl(phenyl)iodonium salts[a]

R	Reaction time (min)	Yield(%)[b]
Bu	30	61
^{t}Bu	40	86
$C_{10}H_{21}$	30	76
	60	78
Cl−$(CH_2)_9$	30	80
^{t}BuC(=O)−$(CH_2)_9$	15	79[c]
MeOOC-$(CH_2)_9$	15	78[c]
AcO-$(CH_2)_9$	60	54

[a] The reaction was carried out as described in the note. [b] Isolated yield based on alkyne used. [c] Isolated as liquid.

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