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

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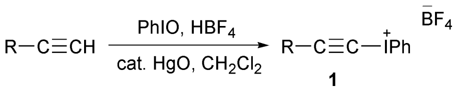
Alkynyliodonium salts can be directly prepared from alk-1-ynes by the reaction with iodosobenzene, tetrafluoroboric acid, and a catalytic amount of HgO.

Alkynyl(aryl)iodonium salts have been recently used as versatile reagents for organic synthesis.[1] They are generally prepared from alk-1-ynes in two-steps *via* the corresponding 1-trimethylsilyl- or 1-trialkylstannyl derivatives.[2] Direct conversion of alk-1-ynes 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 alk-1-ynes with {hydroxy(sulfonyloxy)iodo}arenes, are 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 is 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 alk-1-ynyliodonium salts from alk-1-ynes with a normal alkyl chain without the formation of 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 alk-1-yne was added to the mixture, the yellow color of the aqueous phase faded, and the formation of alk-1-ynyl(phenyl)iodonium salt and the absence of the alk-1-yne and the alkenyliodonium salt could be confirmed from ^1H NMR of the mixture. The alk-1-ynyl(phenyl)iodonium salts could be isolated in good yields as BF_4 salts (Scheme 1).

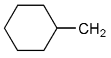


$$R{-}C{\equiv}CH \xrightarrow[\text{cat. HgO, } CH_2Cl_2]{\text{PhIO, } HBF_4} R{-}C{\equiv}C{-}\overset{+}{I}Ph \quad \overset{-}{B}F_4$$

Scheme 1

R. Caple *et al.* succeeded in preparing pentynyl(phenyl)iodonium tetrafluoroborate from pent-1-yne 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 pent-1-yne (*ca.* 40 times) to iodosobenzene tetrafluoroborate. According to our method, various kinds of the alkynyl(phenyl)iodonium salts can be prepared from the corresponding alk-1-ynes. Alkynes having both a normal alkyl group and a sterically hindered one can be converted to the alkynyliodonium salts without a large excess of reagents. Moreover, the introduction of functional groups such as an ester, ketone, or chloride is also possible. (Table 1).† It is a drawback to use a harmful mercury salt but less than 0.5 mol% of HgO is enough to obtain the alkynyliodonium salts in good yield. It is also an advantage of our method that PhIO, HBF_4, and HgO are all commercially available, while iodosobenzene tetrafluoroborate is not.

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

R	Reaction time/min	Yield (%)[b]
Bu	30	61
^tBu	40	86
$C_{10}H_{21}$	30	76
	60	78
Cl-$(CH_2)_9$	30	80
$^tBuC(=O)$-$(CH_2)_9$	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 footnote. [b] Isolated yield based on alkyne used. [c] Isolated as liquid.

Notes and references

† Typical experimental procedure: to a CH_2Cl_2 suspension (2 ml) of iodosylbenzene (132 mg, 0.6 mmol) were added a 42% aqueous solution of HBF_4 (0.62 g, 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, dodec-1-yne (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 remaining 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 dodec-1-ynyl(phenyl)iodonium tetrafluoroborate: white solid, mp 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.

1 P. J. Stang, *Angew. Chem., Int. Ed. Engl.*, 1992, **31**, 274; A. Varvoglis, *The Organic Chemistry of Polycoordinated Iodine*, VCH Publishers, Inc., New York, 1992, pp. 267–277; P. J. Stang and V. V. Zhdankin, *Chem. Rev.*, 1996, **96**, 1123; A. Varvoglis, *Tetrahedron*, 1997, **53**, 1179; M. Ochiai, *Chemistry of Hypervalent Compounds*, ed. K. Akiba, Wiley-VCH, New York, 1999, pp. 359–387.

2 M. Ochiai, M. Kunishima, K. Sumi, Y. Nagao, E. Fujita, M. Arimoto and H. Yamaguchi, *Tetrahedron Lett.*, 1985, **26**, 4501; T. Kitamura and P. J. Stang, *J. Org. Chem.*, 1988, **53**, 4105; P. J. Stang, A. M. Arif and C. M. Crittell, *Angew. Chem., Int. Ed. Engl.*, 1990, **29**, 287; T. Kitamura, M. Kotani and Y. Fujiwara, *Synthesis*, 1998, 1416.

3 (*a*) G. F. Koser, L. Rebrovic and R. H. Wettach, *J. Org. Chem.*, 1981, **46**, 4324; (*b*) L. Rebrovic and G. F. Koser, *J. Org. Chem.*, 1984, **49**, 4700; (*c*) P. J. Stang, B. W. Surber, Z.-C. Chen, K. A. Roberts and A. G. Anderson, *J. Am. Chem. Soc.*, 1987, **109**, 228; (*d*) T. Kitamura, R. Furuki, H. Taniguchi and P. J. Stang, *Tetrahedron*, 1992, **48**, 7149; (*e*) A. B. Sheremetev and E. V. Mantseva, *Tetrahedron Lett.*, 2001, **42**, 5759.

4 V. V. Zhdankin, R. Tykwinski, B. Berglund, M. Mullikin, R. Caple, N. S. Zefirov and A. S. Koz'min, *J. Org. Chem.*, 1989, **54**, 2609.

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