Synthesis of Ethynyl(phenyl)iodonium Tetrafluoroborate. A New Reagent for Ethynylation of 1,3-Dicarbonyl Compounds

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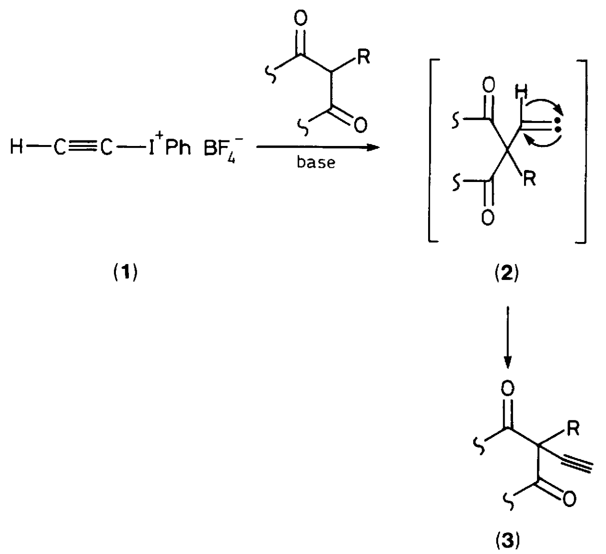
Hydrogen fluoride-induced protiodetrimethylsilylation of trimethylsilylethynyl(phenyl)iodonium tetrafluoroborate (**5**), prepared from bis(trimethylsilyl)ethyne (**4**), affords ethynyl(phenyl)iodonium tetrafluoroborate (**1**), a reagent for α-ethynylation of β-dicarbonyl compounds under mild conditions.

1-Alkynyl(phenyl)iodonium tetrafluoroborates serve as good Michael acceptors toward a variety of nucleophiles.[1] Conjugate addition of enolate anions, derived from 1,3-dicarbonyl compounds, to alkynyliodonium salts generates alkylidenecarbenes as intermediates which undergo intramolecular 1,5-C–H insertion to give cyclopentenes. Phenyl(phenylethynyl)iodonium tetrafluoroborate, however, undergoes phenylethynylation of enolate anions. These results were interpreted in terms of 1,2-migration of the β-phenyl group of the resulting alkylidenecarbene being easier than the intramolecular 1,5-C–H insertion.[1] On the basis of these observations, we have anticipated that ethynyl(phenyl)iodonium tetrafluoroborate (**1**) would undergo ethynylation of enolate anions, derived from 1,3-dicarbonyl compounds, *via* the formation of alkylidenecarbenes (**2**), since the migratory aptitude of the β-hydrogen of alkylidenecarbenes has been shown to be much greater than that of the aryl group (Scheme 1).[2] We report here the synthesis of the unknown salt (**1**) and its reaction with 1,3-dicarbonyl compounds.

Recent studies in our laboratory have shown that the 1-alkynyl(phenyl)iodonium tetrafluoroborates could be synthesized from 1-alkynyltrimethylsilanes by reaction with iodosylbenzene (ISB) and boron trifluoride.[3] The reaction, however, cannot be applied to the synthesis of the most simple analogue (**1**): thus the reaction of trimethylsilylethyn with ISB and boron trifluoride–diethyl ether afforded (*E*)-β-ethoxy-α-trimethylsilylvinyl(phenyl)iodonium tetrafluoroborate instead of the expected salt (**1**).[4] We have developed a new method for the synthesis of (**1**) involving a fluoride-induced protiodetrimethylsilylation of phenyl(trimethylsilylethynyl)iodonium tetrafluoroborate (**5**). Compound (**5**) was prepared from the commercially available bis(trimethylsilyl)ethyne (**4**) in 83% yield, by the reaction with ISB and boron

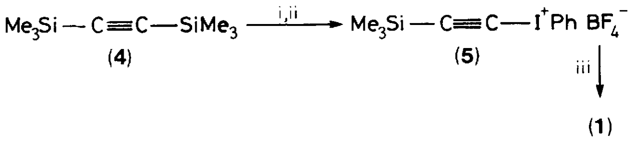


Scheme 1

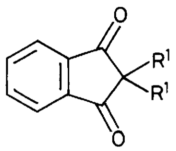
Table 1. Ethynylation using ethynyl(phenyl)iodonium salt (**1**).

Substrate	Reaction conditions Method[a]	Reaction conditions Time/h	Product	Yield[b]/%
(**6a**)	a	2	(**6b**)	74
(**7a**)	c	5.5	(**7b**)	78
(**8a**)	a	3	(**8b**)	71
(**9a**)	b	2	(**9b**)	93[c]
(**10a**)	a	1.5	(**10b**)	63
(**11a**)	c	4	(**11b**)	68
(**12a**)	a	5	(**12b**)	78

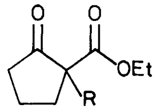
[a] See text. [b] Isolated yield. [c] Yield was determined by ^{1}H NMR spectroscopy.



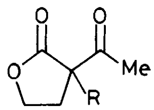
Scheme 2. *Reagents*: i, $(PhIO)_n$, BF_3–Et_2O, CH_2Cl_2; ii, $NaBF_4$; iii, HF, CH_2Cl_2.



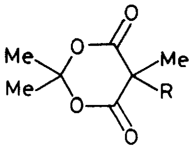
(**6a**) R^1=Me, R^2= H
(**6b**) R^1=Me, R^2= C≡CH
(**6c**) R^1=Me, R^2= C≡CSiMe$_3$
(**7a**) R^1=Ph, R^2= H
(**7b**) R^1= Ph, R^2= C≡CH



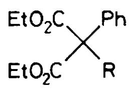
(**8a**) R = H
(**8b**) R = C≡CH



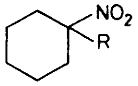
(**9a**) R = H
(**9b**) R = C≡CH



(**10a**) R = H
(**10b**) R = C≡CH



(**11a**) R = H
(**11b**) R = C≡CH



(**12a**) R = H
(**12b**) R = C≡CH

trifluoride in dichloromethane at room temperature, followed by quenching of the reaction mixture with a saturated solution of aqueous sodium tetrafluoroborate (Scheme 2). Treatment of (**5**) with 46% aqueous hydrogen fluoride (2 equiv.) in dichloromethane at room temperature for 30 min gave (**1**) as colourless prisms, m.p. 118—125 °C (decomp.), in 94% yield. The ^{1}H NMR spectrum of (**1**) showed a characteristic singlet assigned to the acetylenic proton at δ 4.38 (1H).[†]

Studies on the *C*-ethynylation of ketone and ester enolates are very limited. Chloroethynylation of enolates with dichloroethyne, followed by reductive dechlorination, results in the formation of α-ethynyl ketones and esters.[5] Recently, Pinhey and co-workers reported a method for the direct ethynylation of β-dicarbonyl compounds, which involves the *in situ* generation of the unstable ethynyl-lead triacetate by the reaction of ethynyltrimethylstannane with lead tetra-acetate.[6] As we expected, the iodonium salt (**1**) underwent ethynylation of β-dicarbonyl compounds (**6a**)—(**11a**) under mild conditions. When enolate anions of β-dicarbonyl compounds (**6a**)—(**11a**), generated by the reaction with KOBu^t (1.2 equiv.) in Bu^{t}OH (method a), KOBu^t (1.1 equiv.) in tetrahydrofuran (THF) (method b), or NaH (1.2 equiv.) in THF (method c), were treated with (**1**) (1.2—1.3 equiv.) at room temperature, α-ethynyl derivatives (**6b**)—(**11b**) were obtained in good yields. Purification of the esters (**8b**) and (**10b**) was carried out using Florisil chromatography due to the unstable nature of the compounds toward silica gel. The results are summarized in Table 1. The potassium salt of nitrocyclohexane (**12a**) also gave the ethyne derivative (**12b**) in 78% yield.

Similarly, with the β-silylethynyliodonium salt (**5**), trimethylsilylethynylation of β-dicarbonyl compounds took place, which is in good agreement with the observation that 1,2-migration of the β-silyl group of β-trimethylsilylcarbenes is a rapid process.[7] For example, reaction of the potassium enolate of (**6a**) with (**5**) in Bu^{t}OH at room temperature for 2 h afforded a mixture of α-trimethylsilylethynyl diketone (**6c**) and (**6a**) in a ratio of 83 : 17 in 83% yield.

While Pinhey ethynylation involves the attack of nucleophiles, derived from dicarbonyl compounds, on an α-acetylenic carbon of ethynyl-lead triacetate, our reaction probably proceeds *via* 1,2-hydrogen migration of alkylidenecarbenes (**2**), produced by the attack of nucleophiles on a β-acetylenic carbon of the ethynyliodonium salt (**1**). Whatever the exact nature of the reaction process, the salt (**1**) will be a useful reagent for the α-ethynylation of β-dicarbonyl compounds.

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[†] *Selected spectroscopic data* for (**1**): IR (nujol) 3250, 2075, 1580, 1565, 1060, 1025, 985, 735, and 670 cm^{-1}; ^{1}H NMR (400 MHz; [^{2}H$_6$]acetone) δ 4.38 (1H, s), 7.72 (2H, m), 7.87 (1H, m), and 8.45 (2H, m); ^{13}C NMR (50 MHz; CD_3OD) δ 30.3 (*C*≡CH), 97.1 (C≡*C*H), 117.3, 133.3, 134.0, and 135.8 (Ph); *m/z* (fast atom bombardment) 229 ($M^+ - BF_4$).