

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

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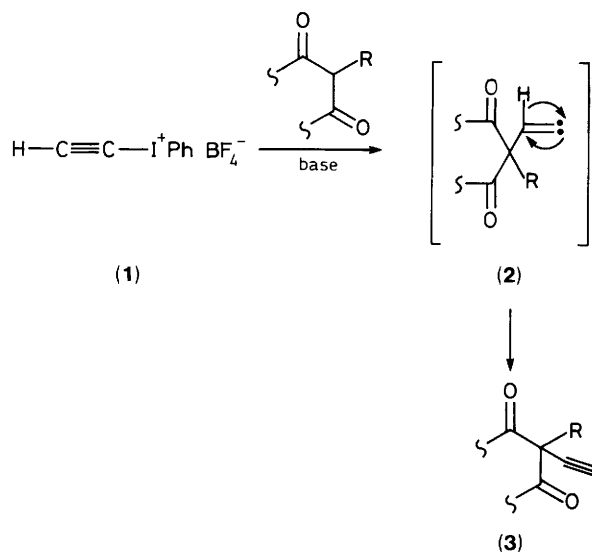
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Hydrogen fluoride-induced protiodetrimethylsilylation of trimethylsilylethynyl(phenyl)iodonium tetrafluoroborate (5), prepared from bis(trimethylsilyl)ethyne (4), affords ethynyl(phenyl)iodonium tetrafluoroborate (1), a reagent for α -ethynylation 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 alkylidene-carbenes as intermediates which undergo intramolecular 1,5-C-H insertion to give cyclopentenones. 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 alkylidene-carbene 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



Scheme 1

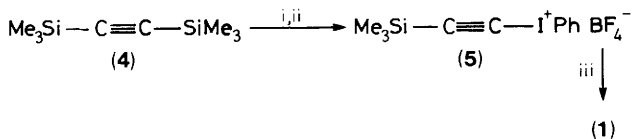
Table 1. Ethynylation using ethynyl(phenyl)iodonium salt (1).

Substrate	Reaction conditions		Product	Yield ^b /%
	Method ^a	Time/h		
(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

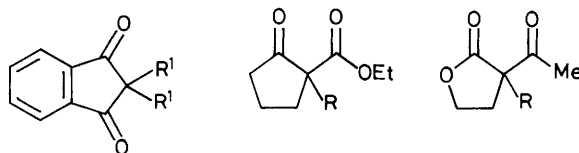
^a See text. ^b Isolated yield. ^c Yield was determined by ¹H NMR spectroscopy.

anions, derived from 1,3-dicarbonyl compounds, *via* the formation of alkylidene-carbenes (2), since the migratory aptitude of the β -hydrogen of alkylidene-carbenes 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 iodobenzene (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 2. Reagents: i, (PhIO)_n, BF₃-Et₂O, CH₂Cl₂; ii, NaBF₄; iii, HF, CH₂Cl₂.



(6a) R¹=Me, R²=H

(8a) R=H

(9a) R=H

(6b) R¹=Me, R²=C≡CH

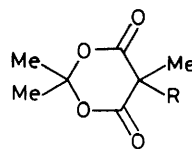
(8b) R=C≡CH

(9b) R=C≡CH

(6c) R¹=Me, R²=C≡CSiMe₃

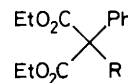
(7a) R¹=Ph, R²=H

(7b) R¹=Ph, R²=C≡CH



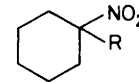
(10a) R=H

(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 ¹H 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^tOH (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^tOH 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; ¹H NMR (400 MHz; [²H₆]acetone) δ 4.38 (1H, s), 7.72 (2H, m), 7.87 (1H, m), and 8.45 (2H, m); ¹³C NMR (50 MHz; CD₃OD) δ 30.3 (C≡CH), 97.1 (C≡CH), 117.3, 133.3, 134.0, and 135.8 (Ph); *m/z* (fast atom bombardment) 229 (*M*⁺ - BF₄).