

Synthesis and Structural Analysis of a Vinylidonium Salt with an α -Silyl Substituent, and Generation of an Iodonium Ylide from it

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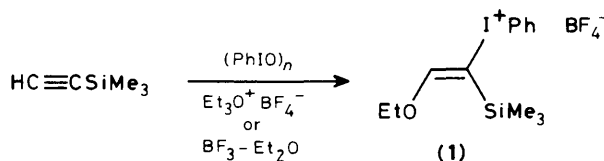
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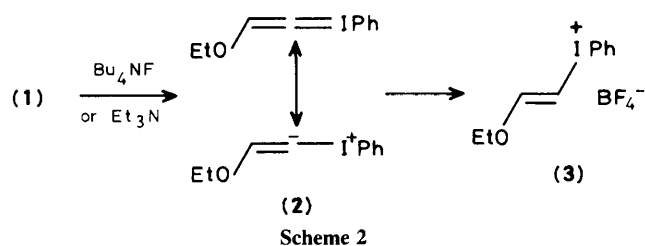
The synthesis and characterization of (*E*)- β -ethoxy- α -trimethylsilylvinyl(phenyl)iodonium tetrafluoroborate (**1**) are described; the product undergoes fluoride ion-induced protidesilylation *via* the formation of the iodonium ylide (**2**).

In spite of numerous studies on the chemistry of stable iodonium ylides of active methylene compounds,¹ little is known about vinylidonium ylides. Recently, the intermediacy of vinyl(phenyl)iodonium ylides that collapse to reactive carbenes with reductive elimination of iodobenzene was proposed in the reaction of alkynyl(phenyl)iodonium salts with nucleophiles such as stable enolate anions and azides.² Stang and his co-workers reported a deuterium exchange reaction of a zwitterionic vinylidone compound with NaOD and suggested the involvement of a vinyl(phenyl)iodonium ylide as a reactive intermediate. They also pointed out that the intermediacy of vinyl anionic species instead of an ylide can account for the results of the base exchange reaction and cannot be ruled out.³ We report here a first synthesis and structure determination of a vinyl(phenyl)iodonium tetrafluoroborate with an α -trimethylsilyl substituent, which serves as a useful progenitor of vinylidonium ylides *via* fluoride ion-induced desilylation.

Reaction of alkynyltrimethylsilanes with Lewis acid-activated iodobenzene causes replacement of the trimethylsilyl group by a phenyliodonium group, and offers an efficient method for the synthesis of alkynyl(phenyl)iodonium salts.⁴



Scheme 1



Scheme 2

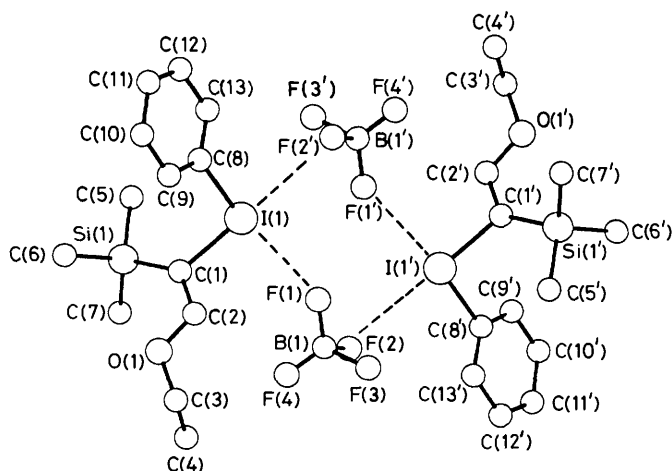


Figure 1. Structure of the bimolecular unit formed around an inversion centre in the crystal of (**1**).

The reaction with trimethylsilylacetylene, however, did not afford the expected ethynyl(phenyl)iodonium salt and resulted in the formation of the α -silylvinylidonium salt (**1**):⁵ treatment of trimethylsilylacetylene with iodobenzene (1.6 equiv.) and triethyloxonium tetrafluoroborate (1.6 equiv.) in dichloromethane at room temperature for 50 h gave stereoselectively (*E*)- β -ethoxy- α -trimethylsilylvinyl(phenyl)iodonium tetrafluoroborate (**1**) as colourless crystals (from dichloromethane-hexane), m.p. 116–118°C, in 68% yield. To our surprise, the use of boron trifluoride-diethyl ether as an alternative to triethyloxonium tetrafluoroborate for the activation of iodobenzene (by co-ordination to the oxygen atom) also afforded the iodonium salt (**1**) in 42% yield. The ¹H n.m.r. spectrum of (**1**) showed a characteristic singlet assigned to the vinylic proton at δ 8.22 (1H).[†]

The double-bond geometry of (**1**) was unambiguously established by single-crystal X-ray diffraction.[‡] The bimolecular unit formed in the crystal of (**1**) (Figure 1) exhibits an

[†] Selected spectroscopic data for (**1**): i.r. (KBr) 1580, 1305, 1200, 1085, and 850 cm⁻¹; ¹H n.m.r. (400 MHz; CDCl₃) δ 0.18 (9H, s), 1.38 (3H, t, *J* 7.0 Hz), 4.33 (2H, q, *J* 7.0 Hz), 7.47 (2H, t, *J* 7.7 Hz), 7.60 (1H, t, *J* 7.7 Hz), 7.90 (2H, m), and 8.22 (1H, s); ¹³C n.m.r. (25 MHz; CDCl₃) δ -0.2 (SiMe₃), 15.2 (CH₂CH₃), 72.1 (CH₂CH₃), 93.8 (=C⁺Ph), 110.6, 131.9, 132.1, and 133.7 (Ph), and 175.5 (=COEt); *m/z* (fast atom bombardment) 347 (*M*⁺ - BF₄).

For (**2**): i.r. (CHCl₃) 1590, 1470, and 1060 cm⁻¹; ¹H n.m.r. (400 MHz; CDCl₃) δ 1.31 (3H, t, *J* 7.0 Hz), 4.07 (2H, q, *J* 7.0 Hz), 6.20 (1H, d, *J* 12.5 Hz), 7.43 (2H, t, *J* 8.0 Hz), 7.56 (1H, t, *J* 7.3 Hz), 7.69 (1H, d, *J* 12.5 Hz), 7.96 (2H, d, *J* 8.0 Hz); ¹³C n.m.r. (25 MHz; CDCl₃) δ 14.3 (CH₂CH₃), 68.6 (CH₂CH₃), 70.6 (=C⁺Ph), 112.4, 132.1, 132.3, and 134.0 (Ph), and 167.3 (=COEt); *m/z* (fast atom bombardment) 275 (*M*⁺ - BF₄).

[‡] Crystal data for (**1**): C₁₃H₂₀OSiIBF₄, *M* = 424.0, triclinic, space group *P* $\bar{1}$, *a* = 11.977(6), *b* = 12.381(7), *c* = 7.059(4) Å, α = 99.03(4), β = 109.59(4), γ = 71.07(3)°, *U* = 931.5(9) Å³, *D*_c = 1.512 g cm⁻³, *Z* = 2, *F*(000) = 408, Mo-K α radiation (λ = 0.71069 Å), μ = 18.4 cm⁻¹. Rigaku diffractometer, 1733 unique reflections collected, range 0.2 \leq 2θ \leq 40.0°; 1611 observed reflections with $|F_o| > 3\sigma(F_o)$. Intensities of 3 standard reflections measured after every 100th scan; the sum of them was reduced to one-half its initial value during data collection within $2\theta = 40^\circ$. Intensity data corrected for decay of the crystal using time-dependent variation of the sum. Structure solved by conventional heavy-atom method, refined by block-diagonal least-squares technique with positional and anisotropic thermal parameters of non-H atoms. H atoms not located in difference electron density map. Final *R*, *R*_w, and *S* values, respectively, 0.069, 0.093, and 1.097 for 1574 reflections. Relatively large *R* value probably due to deterioration of crystal. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

essentially square-planar arrangement with four bonds to iodine [I(1)-C(1), I(1)-C(8), I(1)-F(1), and I(1)-F(2')]. The bond angles C(1)-I(1)-C(8), C(1)-I(1)-F(1), C(8)-I(1)-F(2'), and F(2')-I(1)-F(1) are 97.6(4), 89.8(3), 81.2(4), and 91.3(3)°, respectively. The I-F bond distances of 3.03(1) [to F(1)] and 3.15(1) Å [to F(2')] are significantly larger than the computed covalent single bond length of 1.97 Å, indicating the ionic nature of (**1**).⁶

Protodesilylation of (**1**) proceeds in a completely stereoselective manner with retention of configuration. Under neutral conditions, (*E*)- β -ethoxyvinylidonium tetrafluoroborate (**3**) was obtained by the reaction of (**1**) with tetrabutylammonium fluoride (1.1 equiv.) in tetrahydrofuran (THF) at -78°C, in 63% yield. Reaction with triethylamine (1.2 equiv.) and water (5 equiv.) in dichloromethane at 0°C also afforded (**3**) in 71% yield. The *E*-stereochemistry of (**3**) was shown by the large vicinal coupling constant of 12.5 Hz between vinylic protons.^{†7} Deuterium exchange of (**3**) with triethylamine was carried out in D₂O-THF (1:3) at room temperature and gave α -deuterio-(**3**) in 81% yield (90% deuterium enrichment). These results clearly indicate the intermediacy of the vinylidonium ylide (**2**) in the fluoride ion- and base-induced protodesilylation of (**1**) and also in the deuterium exchange reaction of (**3**).

It appears likely that α -silylvinylidonium salts will be excellent progenitors of vinylidonium ylides under neutral or basic conditions.

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