Stereoselective Synthesis of Highly Labile (*Z*)-β-Alkylvinyl(phenyl)iodonium Perchlorates

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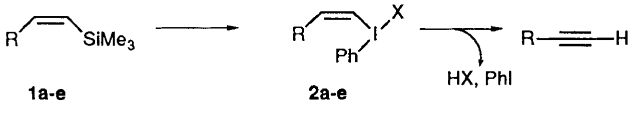
Labile (*Z*)-vinyl(phenyl)iodonium perchlorates **2** (X = ClO_4) were synthesised from (*Z*)-vinylsilanes **1** by the reaction with (diacetoxyiodo)benzene in the presence of BF_3–Et_2O in dichloromethane, followed by quenching with aqueous potassium perchlorate solution.

Nucleophilic vinylic substitution of alkenyl(phenyl)iodonium salts is in general a facile process, mostly because of the super leaving ability of the phenyliodonio group, and provides a useful route for the synthesis of various kinds of alkenes including α-cyano and α-nitro alkenes, vinyl sulphides and sulphones, vinyl halides and vinyl esters.[1] Their α-elimination by base treatment generates alkylidenecarbenes, which undergo an intramolecular 1,5-C–H insertion yielding cyclopentenes.[2] Efficient methods for the synthesis of the alkenyl(phenyl)iodonium salts, however, are limited, especially for the synthesis of (*Z*)-β-alkylvinyl(phenyl)iodonium salts, which are very unstable.[1,3] The facile *anti* β-elimination of (*Z*)-vinyl(phenyl)iodonium salts yielding the corresponding terminal alkynes under either acidic, basic or neutral conditions makes the synthesis of these salts very difficult. The only reported (*Z*)-vinyliodonium salt is bis[(*Z*)-propenyl(phenyl)iodonium] hexachlorostannate, which was prepared by the reaction of (*Z*)-propenyltrichlorostannane with (dichloroiodo)benzene in tetrahydrofuran (THF) at −15 °C in only 5% yield.[4] We report herein a new method for the general synthesis of this labile (*Z*)-vinyl(phenyl)iodonium perchlorates **2** (X = ClO_4).

In the dehydrotrimethylsilylation of (*Z*)-1-(trimethylsilyl)dec-1-ene **1a** with iodosylbenzene activated by triethyloxonium tetrafluoroborate or BF_3–Et_2O yielding dec-1-yne, the intermediate formation of (*Z*)-dec-1-enyl(phenyl)iodonium tetrafluoroborate **2a** (X = BF_4) has been demonstrated by the NMR tube experiment.[1b,5] Furthermore, the experimental results indicate that the rate of formation of **2a** (X = BF_4) under the conditions is comparable to that of the decomposition, *i.e.* reductive *anti* β-elimination of the β-hydrogen and the phenyliodonio group. We found, however, that the use of (diacetoxyiodo)benzene instead of iodosylbenzene decreases the rate of decomposition of the intermediate (*Z*)-dec-1-enyl(phenyl)iodonium salt, presumably the acetate **2a** (X = OAc), and makes the isolation of the labile (*Z*)-iodonium salt possible. To a solution of **1a** (0.5 mmol) and (diacetoxyiodo)benzene (1 equiv.) in dichloromethane was added BF_3–Et_2O (2 equiv.) dropwise at 0 °C under nitrogen and the reaction mixture was stirred for 30 min at 0 °C. Quenching with an aqueous potassium perchlorate (20 equiv.) solution, followed by extraction with dichloromethane and evaporation *in vacuo* gave an oil. These operations should be carried out



a: R = n-C_8H_{17}
b: R = $(Me)_2CH(CH_2)_4$
c: R = cyclo-$C_5H_9CH_2$
d: R = $Ph(CH_2)_3$
e: R = Ph

Scheme 1

Table 1 Synthesis of (*Z*)-vinyliodonium salts **2** and their ^1H NMR parameters

2[a]	Yield[b] (%)	H_α[c]	H_β[c]	^3J[d]
2a	42	7.00	6.61	6.7
2b	22	6.95	6.62	6.5
2c	39	6.95	6.67	6.2
2d	53	6.97	6.60	5.9
2e	30	7.23	7.76	6.3

[a] X = ClO_4. [b] Isolated yield. [c] Chemical shifts of vinylic protons in ppm. [d] Coupling constants between vinylic protons in Hz.

quickly at 0 °C to avoid extensive decomposition of the product. Decantation with hexane at −78 °C several times gave (*Z*)-dec-1-enyl(phenyl)iodonium perchlorate **2a** (X = ClO_4) in 42% yield as crystals, which could be stored at −20 °C for several days without extensive decomposition.†‡

In a similar manner, the (*Z*)-β-alkylvinyl(phenyl)iodonium perchlorates **2b–d** (X = ClO_4) were synthesised from the corresponding (*Z*)-vinylsilanes **1b–d**, which were prepared by hydralumination–protonolysis of 1-(trimethylsilyl)alk-1-ynes using diisobutylaluminum hydride.[6] The (*Z*)-β-phenylvinyliodonium perchlorate **2e** (X = ClO_4) was also prepared in 30% yield. The results are summarised in Table 1, which shows that the (*Z*)-stereochemistry of these salts was determined by the small vicinal coupling constants 5.9–6.7 Hz between two vinylic protons. Large vicinal coupling constants of 13.7–14.2 Hz for (*E*)-vinyl(phenyl)iodonium tetrafluoroborates have been reported.[1b]

The (*Z*)-vinyl(phenyl)iodonium perchlorates **2** (X = ClO_4) are labile both in the solid state and in solution. The rate of decomposition of **2a** (X = ClO_4) in $CDCl_3$ at room temperature, which yields dec-1-yne quantitatively through the reductive *anti* β-elimination, is large and the half-life period is about 20 min. A similar order of half-life period for the other (*Z*)-vinyliodonium perchlorates is observed; 30 min for **2d** and 1 h for **2e**.

The successful synthesis of these (*Z*)-vinyliodonium salts may provide a useful tool to elucidate the chemical reactivity of alkenyliodonium salts.

This work was supported by the Grant-in-Aid for Scientific Research on the Priority Area of Organic Unusual Valency No. 02247101 from the Ministry of Education, Science and Culture, Japan and by Takeda Science Foundation.

Received, 27th March 1991; Com. 1/01466H

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† *Selected spectroscopic data* for **2a** (X = ClO_4): m.p. 32–34 °C (decomp.); IR ν_{max}/cm^{-1} (Nujol) 3070, 1605, 1560, 1290, 1270, 1120–1020, 980, 920, 900, 825, 725 and 665; ^1H NMR (270 MHz; $CDCl_3$) δ 0.88 (3H, t, *J* 6.6 Hz), 1.10–1.62 (12H), 2.43 (2H, q, *J* 6.7 Hz), 6.61 (1H, q, *J* 6.7 Hz), 7.00 (1H, d, *J* 6.7 Hz), 7.49 (2H, t, *J* 7.8 Hz), 7.63 (1H, t, *J* 7.3 Hz), and 7.98 (2H, d, *J* 7.8 Hz).

‡ **CAUTION**: Iodonium perchlorates are inherently explosive and the large scale preparation of these salts should be avoided. (We found that 1 g of phenyl(phenylethynyl)iodonium perchlorate exploded after standing at room temp. for less than 30 min.)