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Evidence for Michael-Type Reaction of Alkenyliodonium Salts: Nucleophilic Substitutions with Sodium Benzenesulfinate

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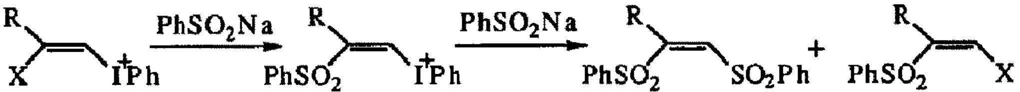
Abstract: Nucleophilic vinylic substitutions of (Z)-(β-haloalkenyl)iodonium tetrafluoroborates with sodium benzenesulfinate yielding (Z)-1,2-bis(phenylsulfonyl)alkenes will involve Michael-type addition of the nucleophile to the alkenyliodonium salts at the C_β atom.

Alkynyliodonium salts are highly electron deficient species and act as a good Michael acceptor toward the attack of nucleophiles, which makes possible an efficient cyclopentene annulation via the tandem Michael addition-carbene insertion reaction.[1] Michael-type addition to alkenyliodonium salts at the C_β atom, however, has never been observed.[2] We report herein evidence supporting that nucleophilic vinylic substitutions of (Z)-(β-haloalkenyl)iodonium tetrafluoroborates with sodium benzenesulfinate will involve a Michael-type addition as the first step of the reaction and afford the retained (Z)-1,2-bis(phenylsulfonyl)alkenes stereoselectively in high yields.



1: X = Cl
2: X = Br

3: Y = BF_4, $PhSO_2$, or X

4

5: X = Cl
6: X = Br

a: R = Me
b: R = n-C_8H_{17}
c: R = cyclo-$C_5H_9CH_2$
d: R = $ClCH_2(CH_2)_2$
e: R = $Ph(CH_2)_2$

Exposure of (Z)-(2-chloro-1-decenyl)iodonium tetrafluoroborate (**1b**)[3] to sodium benzenesulfinate (2.5 equiv.) in THF at 0 °C for 2 h gave the (Z)-1,2-bis(phenylsulfonyl)alkene **4b**[4] in 92% yield, along with the formation of trace amounts of the (Z)-chlorosulfone **5b**.[5] Similarly, the reaction with the β-chlorovinyliodonium salts **1a**, **1c**, **1d**, and **1e** afforded the corresponding (Z)-bis(phenylsulfonyl)alkenes **4a** (95%), **4c** (87%), **4d** (93%), and **4e** (91%), respectively. In marked contrast, the reaction of (Z)-(2-bromo-1-decenyl)iodonium salt **2b** resulted in formation of a large amount of the (Z)-bromosulfone **6b**,[5] and afforded a 63:37 mixture of **4b** and **6b** in 82% yield. All of these reactions are exclusively stereoselective (by ^{1}H NMR) with retention of configuration.

These nucleophilic vinylic substitutions will involve hitherto unknown Michael-type addition to the alkenyliodonium salts at the C_β atom. Figure 1 shows the time courses of the reaction of **1b** with sodium

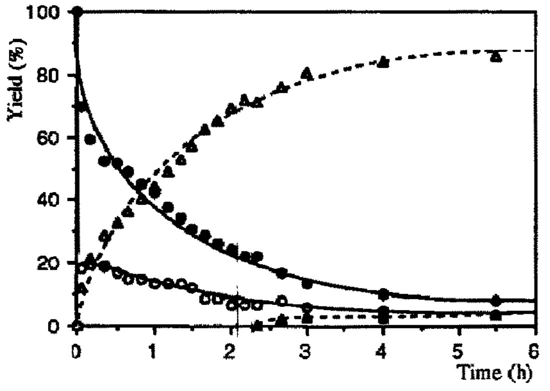


Figure 1. Time courses of the reaction of (Z)-(2-chloro-1-decenyl)iodonium tetrafluoroborate **1b** with sodium benzenesulfinate (2.5 equiv.) in CDCl$_3$ at room temperature. Yields were determined by ^{1}H NMR. Symbols are % recovered **1b** (●), **3b** (○), **4b** (△), and **5b** (▲).

benzenesulfinate in CDCl$_3$ at room temperature. Changing the solvent from THF to CDCl$_3$ slows down the rate of the reactions. Most importantly, the formation of the (*Z*)-(β-(phenylsulfonyl)alkenyl)iodonium salt **3b**[6] was observed, especially at the early stage of the reaction. The amounts of **3b** gradually decrease with an increase in the yields of the 1,2-bis(phenylsulfonyl)alkene **4b**, indicating that **3b** is an intermediate leading to **4b**. It has been shown that nucleophilic vinylic substitutions of **3b** (Y = BF$_4$) with sodium benzenesulfinate proceed at 0 °C in THF with retention of configuration and afford **4b** selectively.[4] This substitution of **3b** with sodium benzenesulfinate would compete with the attack of chloride ion, liberated upon the formation of **3b** from **1b**: thus, formation of a small amount of (*Z*)-chlorosulfone **5b**, produced by nucleophilic substitution of **3b** with chloride ion,[5] was observed at the late stage of the reaction. These are in good agreement with the result, obtained by competitive experiments,[7] that the rate of substitution of **3b** with benzenesulfinate ion is noticeably larger than that with chloride ion. When the reaction of **1b** was carried out using 1 equiv. of sodium benzenesulfinate in THF (0 °C, 3 h) and quenched with an aqueous NaBF$_4$ solution, a mixture of **1b** (26%), 3b (Y = BF$_4$, 6%), **4b** (34%), and **5b** (<1%) was produced.

Michael-type addition of sodium benzenesulfinate to **1b** followed by chloride ion extrusion will lead to the formation of **3b** with retention of configuration. An alternative route to **3b** involving generation of 1-decynyl(phenyl)iodonium salt from **1b** by *anti* β-elimination of HCl, followed by the Michael-type addition of sodium benzenesulfinate, does not seem to be important, since the reaction of 1-decynyl(phenyl)iodonium salt with sodium benzenesulfinate will directly generate an (α-(phenylsulfonyl)alkylidene)carbene and not produce **3b**.[6] Time courses of the reaction of (*Z*)-β-bromovinyliodonium salt **2b** with sodium benzenesulfinate in CDCl$_3$ also show the formation of the (*Z*)-(β-(phenylsulfonyl)alkenyl)iodonium salt **3b** as an intermediate and provide an additional evidence for Michael-type addition to the alkenyliodonium salts.

References and Notes

1. Ochiai, M.; Kunishima, M.; Nagao, Y.; Fuji, K.; Shiro, M.; Fujita, E. *J. Am. Chem. Soc.* **1986**, *108*, 8281.
2. Varvoglis, A *The Organic Chemistry of Polycoordinated Iodine*; VCH Publishers, Inc.: New York, 1992.
3. Ochiai, M.; Uemura, K.; Oshima, K.; Masaki, Y.; Kunishima, M.; Tani, S. *Tetrahedron Lett.* **1991**, *32*, 4753.
4. Ochiai, M.; Oshima, K.; Masaki, Y.; Kunishima, M.; Tani, S. *Tetrahedron Lett.* **1993**, *34*, 4829.
5. Ochiai, M.; Oshima, K.; Masaki, Y. *Tetrahedron Lett.* **1991**, *32*, 7711.
6. Ochiai, M.; Kunishima, M.; Tani, S.; Nagao, Y. *J. Am. Chem. Soc.* **1991**, *113*, 3135.
7. Moreover, no interconversion between 4b and 5b under the reaction conditions was confirmed.

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