

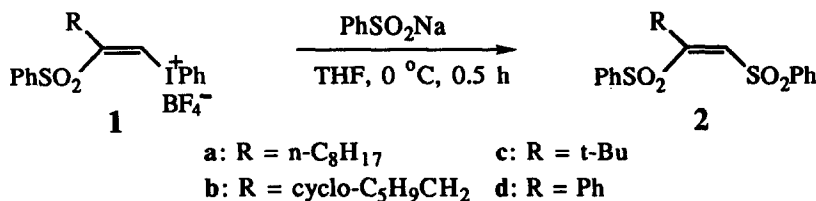
Nucleophilic Vinylic Substitutions of (Z)-(β -(Phenylsulfonyl)-alkenyl)iodonium Tetrafluoroborates with Sodium Benzenesulfinate: Stereoselective Synthesis of (Z)-1,2-Bis(phenylsulfonyl)alkenes

Masahito Ochiai,^{a,*} Kunio Oshima,^b Yukio Masaki,^b
Munetaka Kunishima,^c and Shohei Tani^c

Faculty of Pharmaceutical Sciences,^a University of Tokushima, 1-78 Shomachi, Tokushima 770, Japan
Gifu Pharmaceutical University,^b 5-6-1 Mitahora Higashi, Gifu 502, Japan
Faculty of Pharmaceutical Sciences,^c Kobe Gakuin University, Nishi-ku, Kobe 673, Japan

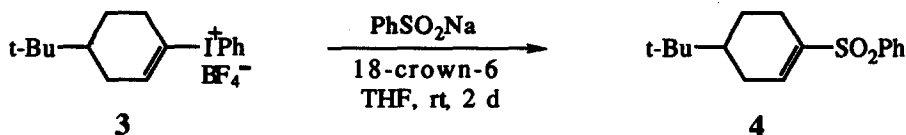
Abstract: Nucleophilic vinylic substitutions of (Z)-(β -(phenylsulfonyl)alkenyl)iodonium tetrafluoroborates with sodium benzenesulfinate afford (Z)-1,2-bis(phenylsulfonyl)alkenes with retention of stereochemistry in good yields.

Electron deficient 1,2-bis(phenylsulfonyl)alkenes serve efficiently as both Michael acceptors and 2π partners in cycloaddition reactions.¹ The two sulfonyl groups of the Diels-Alder adducts can be reductively removed under mild conditions to the corresponding olefins. We report herein a nucleophilic vinylic substitution of (Z)-(β -(phenylsulfonyl)alkenyl)iodonium tetrafluoroborates **1** with sodium benzenesulfinate, which gives the retained (Z)-1,2-bis(phenylsulfonyl)alkenes **2** stereoselectively in good yields.

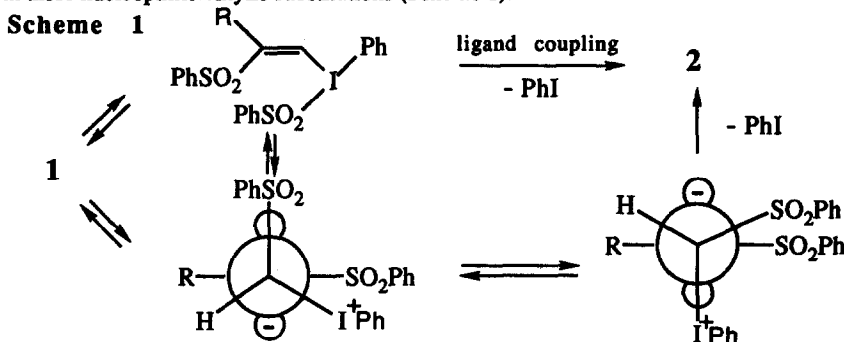


Nucleophilic substitutions at vinylic carbons of simple (*E*)-(β -alkylvinyl)iodonium tetrafluoroborates with *n*-Bu₄NX (X = Cl, Br, and I) proceed with exclusive inversion of configuration, presumably via S_N2 type transition state.² In the reaction of **1** with *n*-Bu₄NX, however, exclusive retention of stereochemistry leading to the formation of (Z)- β -(phenylsulfonyl)vinyl halides was observed.³ Exposure of (Z)-2-(phenylsulfonyl)-1-decenyl)iodonium tetrafluoroborate **1a**³ to sodium benzenesulfinate (1.1 equiv.) in THF at 0 °C for 0.5 h gave the 1,2-bis(phenylsulfonyl)alkene **2a** quantitatively. Similarly, the reaction with the alkenyliodonium salts **1b**, **1c**, and **1d** afforded the corresponding bis(phenylsulfone) **2b** (85%), **2c** (76%), and **2d** (68%), respectively. Polymer supported benzenesulfinate anion also undergoes the nucleophilic vinylic substitutions of **1**: treatment of **1a** with Amberlyst A-26, benzenesulfinate form,⁴ (10 equiv.) in CH₂Cl₂ at room temperature for 1 h gave

2a in 92% yield. All of these reactions are exclusively stereoselective (by NMR) with retention of configuration. The *Z* stereochemistry of **2a** and **2b** was established by the observation of a nuclear Overhauser effect (NOE) enhancement (5% and 7%) between the vinylic and allylic protons. The vinylic substitution of the cyclic vinylidonium tetrafluoroborate **3**⁵ with sodium benzenesulfinate in THF gave poor results and the corresponding vinyl sulfone **4** was obtained in 29% yield.⁶ In the presence of 18-crown-6, however, the reaction was much improved and **4** was obtained in 80% yield.



Both an addition-elimination route⁷ and a ligand coupling mechanism⁸ on iodine(III) of the intermediate iodonium benzenesulfonates produced by ligand exchange are compatible with the stereochemical outcome observed in these nucleophilic vinylic substitutions (Scheme 1).



Acknowledgment. This work was supported in part by the Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture, Japan.

References and Notes

- (a) Lucchi, O. D.; Pasquato, L. *Tetrahedron* **1988**, *44*, 6755. (b) Cossu, S.; Lucchi, O. D.; Fabbri, D. *Org. Prep. Proc. Int.* **1991**, *23*, 571.
- Ochiai, M.; Oshima, K.; Masaki, Y. *J. Am. Chem. Soc.* **1991**, *113*, 7059.
- Ochiai, M.; Oshima, K.; Masaki, Y. *Tetrahedron Lett.* **1991**, *32*, 7711.
- Manescalchi, F.; Orena, M.; Savoia, D. *Synthesis* **1979**, 445.
- Ochiai, M.; Sumi, K.; Nagao, Y.; Fujita, E. *Tetrahedron Lett.* **1985**, *26*, 2351.
- (a) Nesmeyanov, A. N.; Tolstaya, T. P.; Petrakov, A. V.; Goltsev, A. N. *Dokl. Akad. Nauk SSSR* **1977**, *235*, 591. (b) Nesmeyanov, A. N.; Tolstaya, T. P.; Petrakov, A. V.; Leshcheva, I. F. *Dokl. Akad. Nauk SSSR* **1978**, *238*, 1109.
- (a) Rappoport, Z. *Adv. Phys. Org. Chem.* **1969**, *7*, 1. (b) Modena, G. *Acc. Chem. Res.* **1971**, *4*, 73. (c) Miller, S. I. *Tetrahedron* **1977**, *33*, 1211. (d) Rappoport, Z. *Acc. Chem. Res.* **1981**, *14*, 7. (e) Rappoport, Z. *Recl. Trav. Chim. Pays-Bas* **1985**, *104*, 309. (f) Shainyan, B. A. *Usp. Khim.* **1986**, *55*, 942.
- Oae, S.; Uchida, Y. *Acc. Chem. Res.* **1991**, *24*, 202.