

테트라부틸암모늄 술포네이트 : 올레핀으로부터 비닐술포의 합성을 위한 편리한 시약

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Tetrabutylammonium Sulfinate: A Reagent for Facile Synthesis of Vinyl Sulfones from Olefins

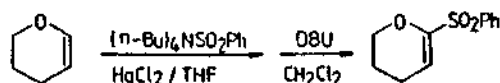
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Although olefin itself is a versatile and useful functional group for organic synthesis, its versatility and uniqueness as the synthetic intermediate would be augmented if pathways for transformation of the simple olefin into the activated olefin such as the vinyl sulfone are readily available. In conjunction with our work on β -hydroxysulfonyl sugars¹, we were interested in the facile synthesis of vinylsulfones.

Selenosulfonation of olefins and the subsequent elimination has been documented for the conversion of olefins to vinylsulfones²⁻⁵ in early 1980's. Although solvomercuration-demercuration methodologies for the synthesis of functionalized olefins have been well known, we were surprised to find only one report by Sas for the synthesis of vinylsulfones employing the sulfonylmercuration-demercuration method.⁶

We followed the procedure of Sas⁶ for the sulfonylmercuration, in which a mixture of olefin, mercuric chloride, and sodium benzenesulfinate is stirred in water, but method was not satisfactory for certain olefins such as norbornene and dihydropyran probably because of the low solubility of norbornene and the sensitivity of dihydropyran in aqueous solution. In order to conduct the mer-

curosulfonation in organic solvents, sodium benzenesulfinate must be replaced by other sulfinate salts which are soluble in organic solvents. Mercuric chloride is quite soluble in ether or THF. Therefore, we prepared tetrabutylammonium benzenesulfinate, which is indeed soluble in organic solvents. Thus, a mixture of sodium benzenesulfinate (1.21 g) and Amberlite IRA-400 (2 g) was vigorously stirred for 3 hr at room temperature. A column was packed with this stirred mixture and was eluted with the aqueous solution (100 ml) of tetrabutylammonium bromide (2.39 g) employing a micropumping system (elution rate; 100 ml/30 min). The collected aqueous solution was extracted with methylene chloride and solvent was evaporated to give pure tetrabutylammonium benzenesulfinate.⁷ Mercurosulfonation of various olefins with $(n\text{-Bu})_4\text{SO}_2\text{Ph}$ in organic solvent was quite facile and successful mercurosulfonations of dihydropyran and norbornene were achieved.



A typical example is the mercurosulfonation-demercuration of norbornene. A mixture of nor-

bornene (0.47 g, 5 mmol), (*n*-Bu)₄NSO₂Ph (1.92 g, 5 mmol) and HgCl₂ (1.36 g, 5 mmol) in dry THF (25 ml) was stirred at room temperature under nitrogen atmosphere for 1 hr. The reaction mixture was partitioned between methylene chloride and water. The organic layer was dried and evaporated to give the crude product which was demercurated with sodium methoxide (0.5 g) in methanol (20 ml)-methylene chloride (5 ml) solution. After stirring at room temperature for 2 hr, the reaction mixture was filtered and was partitioned between methylene chloride and water. The organic layer was washed with water, dried, evaporated to dryness and the residue was purified by column chromatography to give the pure vinyl sulfone (0.87 g, 62 %). Usually, the demercuration is almost quantitative regardless of bases such as sodium hydroxide, sodium alkoxide, triethylamine, or DBU. In the case of 3, 4-dihydro-2H-pyran which could produce two regioisomers in theory, 3, 4-dihydro-6-phenylsulfonyl-2H-pyran was the major isomer and very small amount of the other isomer was produced. This mercurosulfonation-demercuration procedure employing (*n*-

Bu)₄NSO₂Ph was also successful for other simple olefins such as cyclopentene, cyclohexene and 3-hexene. Regiochemistry of the mercurosulfonation step is currently under investigation.

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인 용 문 헌

1. K. S. Kim, J. K. Sohng, S. B. Ha, C. S. Cheong, and C. S. Hahn, *Tetrahedron Lett.*, **29**, 2847 (1988).
2. T. G. Back and S. Collins, *Tetrahedron Lett.*, **21**, 2215 (1980).
3. R. A. Gancarz and J. L. Kice, *Tetrahedron Lett.*, **21**, 4155 (1980).
4. T. Miura and M. Kobayashi, *J. C. S. Chem. Commun.*, 438 (1982).
5. L. A. Paquette and G. D Course, *J. Org. Chem.*, **48**, 141 (1983).
6. W. Sas, *J. C. S. Chem. Commun.*, 862 (1984).
7. Tetrabutylammonium benzenesulfonate: mp 99 °C; IR (KBr) 1050 cm⁻¹; ¹H NMR (CDCl₃) δ 0.9-1.4 (m, 28H), 3.1-3.3 (m, 8H), 7.2-7.8 (m, 5H).