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(7) All amino acids except glycine are of the L configuration unless noted. Standard abbreviation for amino acids, protecting groups, and peptides recommended by the IUPAC-IUB Commission on the Biochemical Nomenclature (*J. Biol. Chem.*, **247**, 977 (1972)) are used. Additional abbreviations follow: BOC, *tert*-butoxycarbonyl; Phe[(Z)Δ], (*Z*)-dehydrophenylalanine; Phe[3SBzl], 3-benzylthiophenylalanine; Aᵗbu, α-aminoisobutyric acid; pMZ, *p*-methoxybenzyloxycarbonyl.
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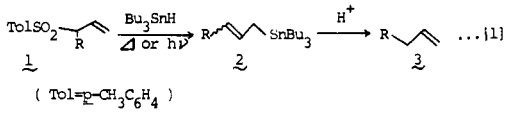
## Regioselective Desulfonylation of Allylic Sulfones with Organotin Hydride Involving Double Migration of the Double Bond[1]

*Sir:*

Allylic sulfides, sulfoxides, or sulfones have been proven to be valuable synthetic intermediates for carbon-carbon bond formation via the sulfur-stabilized carbanions.[2,3]

In contrast to the various efforts to improve the regioselectivity in such allylic alkylation (α vs. γ),[3] little attention has been directed toward improving the regioselectivity in the reductive desulfurization process of the resulting allylic alkylated sulfur compounds.[4]

In connection with our recent finding on the desulfurizative stannylation of propargyl (or allyl) sulfides via an $S_H'$ process,[5] we report here the completely regioselective desulfonylation of allylic sulfones to energetically less stable terminal olefins with tri-*n*-butyltin hydride involving double migration of double bond as outlined in eq 1.




... (1)

Thus, α-alkylated allyl tolyl sulfone (**1**)[4a,6] reacted with twice the molar amount of tri-*n*-butyltin hydride[7] in the presence of the catalytic amount of azobisisobutyronitrile (AIBN) in refluxing benzene for 2 h to afford allyltin derivatives (**2**) in good isolated yield.[8] The same stannylated products (**2**) were also obtained by a photochemical procedure at room temperature for ~10 h (see Table II).

In both cases, the reaction was conveniently followed by the disappearance of the absorptions of tin hydride (1800 $cm^{-1}$) and sulfone (1315 ± 5, 1145 ± 5 $cm^{-1}$) and also the appearance of the new band at 960 and 980 $cm^{-1}$ ($TolSO_2SnBu_3$)[8] in the IR spectrum. All allyltins obtained here were a mixture of trans and cis isomers.[9] The results of the thermal reaction are summarized in Table I.

**Table I.** Allyl Transfer from Sulfur to Tin

| Sulfone | Product[10] | Yield (%)[a] |
|---|---|---|
| 1a TolSO2 | 2a SnBu3 | 68 |
| 1b TolSO2 | 2b SnBu3 | 65 |
| 1c TolSO2 | 2c SnBu3 | 68 |
| 1d TolSO2, Ph | 2d Ph, SnBu3 | 74 |
| 1e SO2Tol | 2e SnBu3 | 71 |

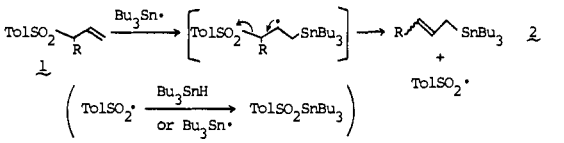
[a] Isolated yield.

**Table II.** Desulfonylation of Allylic Sulfones

| Sulfone | Product | Yield (%)[a] method A[b] | method B[c] |
|---|---|---|---|
| 1a TolSO2 | 3a | 80 | 57 |
| 1b TolSO2 | 3b | 80 | 66 |
| 1c TolSO2 | 3c | 87 | 62 |
| 1d TolSO2, Ph | 3d Ph | 84 | 73 |
| 1e SO2Tol | 3e | 46[d] | 26[d] |

[a] Yields were determined by GC analysis. [b] Method A: thermal reaction in refluxing benzene for 2 h in the presence of AIBN. [c] Method B: photoreaction in degassed benzene solution for 10 h at room temperature using a Pyrex tube (100-W high-pressure mercury lamp). [d] Isolated yield.

The possible reaction scheme may be best explained in terms of the $S_H'$ process similar to the allenyl transfer from propargyl sulfide.[5]




The present reaction provides a new general synthetic method for the preparation of allyltins. In view of the possible variation of the substituents (R),[4a] the method seems to have an advantage over the existing one, in which allylic Grignard reagents are generally employed.[11]

The present facile stannylation reaction, when combined with the ease protolysis of allyltins,[12] offers a unique methodology, in which the completely regioselective desulfonylation of allylic sulfones becomes available.

Thus we investigated the one-pot desulfonylation without isolation of allyltin species. Treatment of the above reaction mixture with concentrated hydrochloric acid or acetic acid produced terminal olefins (**3**) in good yield without contamination of internal ones (see eq 1). The results are summarized in Table II.

This is a first example of the completely regioselective desulfurization of allylic sulfones to energetically less stable terminal olefins in contrast to the method of Umani-Ronchi et al.[4a,13] Moreover, it is quite apparent that other electrophiles[14] besides the proton can be used in the destannylation step to generate other functional alkenes. α-Alkylation, followed by stannylation of allyl sulfones, and subsequent destannylation with various electrophiles provide an attractive entry to the preparation of functional alkenes in a completely regioselective manner.

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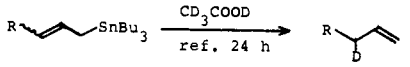
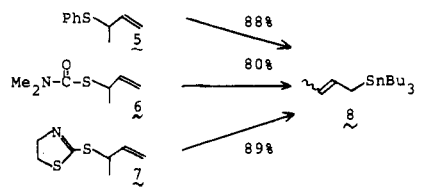
As an additional example, we demonstrated the preparation of deuterated alkenes **4a** and **4b** using acetic-$d_3$ acid-$d$.



4a, R=PhCH$_2$ 55%

4b, R=CH$_3$(CH$_2$)$_7$ 76%

The usefulness of the present concept for the completely regioselective allylic desulfurization to terminal olefins will be further enhanced if allylic sulfur compounds other than sulfones can be generally transfered to allyltins. This was realized in the following allylic sulfides under similar conditions.[18]



The ready availability of tri-*n*-butyltin hydride from inexpensive starting materials and the facility of the reaction provide a stimulus for further exploration of its chemistry and the chemistry of allyltins.

A typical procedure[19] is as follows. A mixture of 3-tolylsulfonylnona-1-ene (**1b**, 447 mg, 1.38 mmol), tri-*n*-butyltin hydride (928 mg, 3.19 mmol), and AIBN (~10 mg) in dry benzene (3 mL) was refluxed under a nitrogen atmosphere for 2 h until the disappearance of the absorption of sulfone at 1320 and 1150 cm$^{-1}$. After the completion of the reaction, 1-(tri-*n*-butylstannyl)nona-2-ene (**2b**) was isolated by column chromatography (neutral alumina, eluted with benzene) in 65% yield (443 mg) as a colorless oil. The further purification was carried out by Kugelrohr distillation under reduced pressure: bp 136-142 °C (0.003 mm).

Protolysis of the crude reaction mixture was carried out using concentrated hydrochloric acid (3 mL) or acetic acid (3 mL) at room temperature for several hours. 1-Alkenes **3** were identified by the comparison of GC analysis and spectral data with those of authentic samples.

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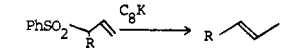
(3) (a) K. Narasaka, M. Hayashi, and T. Mukaiyama, *Chem. Lett.*, 259 (1972); (b) K. Hirai and Y. Kishida, *Tetrahedron Lett.*, 2743 (1972); (c) T. Nakai, H. Shiono, and M. Okawara, *Chem. Lett.*, 249 (1975); (d) T. Hayashi and H. Midorikawa, *Synthesis*, 100 (1975).

(4) Reductive desulfurization of allylic sulfur compounds, especially possessing a terminal double bond, generally gave a mixture of internal and terminal olefins involving double-bond migration; see ref 3 and 2b. In the case of



the following sulfones, complete double-bond migration has been reported: (a) D. Savoia, C. Trombini, and A. Umani-Ronchi, *J. Chem. Soc., Perkin Trans. 1*, 123 (1977). On the other hand, allylic sulfones bearing an internal double bond have been desulfurized without double-bond migration with LiEtNH$_2$; e.g., see (b) B. M. Trost, L. Weber, P. Strege, T. J. Fullerton, and T. J. Dietsch, *J. Am. Chem. Soc.*, **100**, 3426 (1978).

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(6) **1a:** mp 43-44 °C (*n*-hexane). **1b:** mp 53-54 °C (ether-*n*-hexane). **1c:** mp 68-69 °C (CCl$_4$). **1d:** mp 95-96 °C (ether-*n*-hexane). **1e:** 210-215 °C (0.003 mm) Kugelrohr).

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(8) Tolylsulfonyl moiety was trapped by tin hydride to give tri-*n*-butyltolylsulfonylstannane (Bu$_3$SnSO$_2$Tol). The IR absorptions at 960 and 980 cm$^{-1}$ suggest the sulfinate structure. Cf. W. Kitching, C. N. Fong, and A. J. Smith, *J. Am. Chem. Soc.*, **91**, 767 (1969).

(9) The stereochemistry of allyltins **2** was tentatively determined by its $^{13}$C NMR spectrum measured under the conditions of the minimum NOE influence and pulse repetition, 4.5 s. For example, the spectrum of **2b** showed the $\beta$ carbon to the butyltin group at $\delta$ 128.89 and 128.01 (integration, 71:29), and the $\alpha$ carbon at $\delta$ 125.97 and 124.56 (integration, 70:30) indicative of its trans:cis ratio being ~70:30. Similar ratios were obtained for **2a, 2c,** and **2d.**

(10) Kugelrohr distillation. **2a:** bp 132-138 °C (0.002 mm). **2b:** bp 136-142 °C (0.003 mm). **2c:** 162-168 °C (0.002 mm). **2d:** bp 186-196 °C (0.002 mm). **2e:** 175-185 °C (0.003 mm).

(11) D. Seyferth and M. A. Weiner, *J. Org. Chem.*, **24**, 1395 (1959).

(12) Easy protolysis of allyltins is well known; see J. A. Verdone, J. A. Mangravite, M. Scarpa, and H. G. Kuivila, *J. Am. Chem. Soc.*, **97**, 843 (1975); S. J. Hannon, T. G. Tralor, *J. Chem. Soc., Chem. Commun.*, 630 (1975).

(13) $\gamma$-Alkylated allylic sulfones such as crotyl tolyl sulfone did not react with tri-*n*-butyltin hydride. This result is consistent with the observation that organotin hydride generally affords hydrostannylated products toward terminal olefins but not internal olefins: N. P. Neumann and R. Sommer, *Justus Liebigs Ann. Chem.*, **675**, 10 (1964).

(14) For example, a wide variety of electrophiles such as alkyl halides,[15] aldehydes,[16] or pentacarbonylmanganese halide[17] are known to react with allyltins to produce functional alkenes.

(15) J. Grignon, C. Serves, and M. Pereyre, *J. Organomet. Chem.*, **96**, 225 (1975).

(16) G. Cainelli, G. Cardillo, M. Contento, G. Trapani, and A. Umani-Ronchi, *J. Chem. Soc., Perkin Trans. 1*, 400 (1973).

(17) E. W. Abel and R. J. Rowley, *J. Chem. Soc., Chem. Commun.*, 72 (1974).

(18) Allylic sulfoxides, however, fail to give allyltin compounds, presumably owing to their facile [2,3]-sigmatropic rearrangement. See ref 2a.

(19) All new compounds obtained here had satisfactory physical and spectral data as well as elemental analyses.



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## $^{15}$N NMR of *cis*-Diamine-Platinum(II) Complexes in Aqueous Solution[1]

*Sir:*

The recent interest in the aqueous chemistry of *cis*-diamine-platinum(II) compounds is the result of the discovery by Rosenberg and co-workers[2] in 1969 that *cis*-dichlorodiammineplatinum(II) (DDP) is an antitumor agent. Although DDP and similar compounds have been shown to inhibit DNA synthesis, the exact mode of biological action of these compounds is not known[3] despite a great number of studies of these anticancer agents and their interaction with biomolecules.[4] This has prompted us to explore the potential of $^{15}$N magnetic resonance as a probe for determining the biological binding site of these Pt(II) species. Studies have suggested that the uncharged DDP species diffuses through the cell membrane but, once in the cell, dissociates $Cl^-$ to form *cis*-$(NH_3)_2Pt(H_2O)_2^{2+}$ which may then attack one or more basic nitrogen sites of the purine or pyrimidine bases in the nucleic acid chain.[5] We have accordingly prepared and recorded $^{15}$N spectra for aqueous solutions of *cis*-$(^{15}NH_3)_2Pt(H_2O)_2^{2+}$ (**1**), $^{15}$N-enPt$(H_2O)_2^{2+}$ (**3**) ($^{15}$N-en = 100% $^{15}$N-labeled ethylenediamine) and for derivatives of **1** and **3** in which one or both $H_2O$ molecules are replaced by 100% $^{15}$N-labeled 1-methylimidazole ($^{15}$N-MeIm). We have found that replacement of $H_2O$ by $^{15}$N-MeIm in the Pt(II) complexes produces a large change in both the $^{15}$N chemical shift and the $^{195}$Pt-$^{15}$N coupling constant for the $^{15}NH_3$ or $^{15}$N-en nitrogens. At the same time, the $^{15}$N resonances for both $^{15}N_1$ and $^{15}N_3$ of the $^{15}$N-MeIm are shifted from their positions in an aqueous solution of $^{15}$N-MeIm and both resonances display satellites due to $^{195}$Pt-$^{15}$N coupling. These results indicate that $^{15}$N NMR is a sensitive probe for detecting interactions between *cis*-diamine-platinum(II)$^{2+}$ species and imidazole-ring nitrogen in biological systems (e.g., purine base sites of nucleic acids)

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