cently been reported. An interpretation involving thiol activation in the attack on the flavin-thiol intermediate is consistent with the mechanisms discussed in this paper for the flavin-thiol reaction in the absence of micelles: S. Shinkai, R. Ando, and T. Kunitake, *J. Chem. Soc., Perkin Trans. 2*, 1271 (1978).

[12] National Science Foundation Undergraduate Research Participant.

J. M. Sayer,* P. Conlon, J. Hupp,[12] J. Fancher,
R. Belanger, E. J. White
Department of Chemistry, University of Vermont
Burlington, Vermont 05405

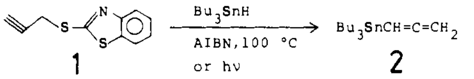
Received November 14, 1978

Desulfurizative Stannylation of Propargylic or Allylic Sulfides via an S_H' Process

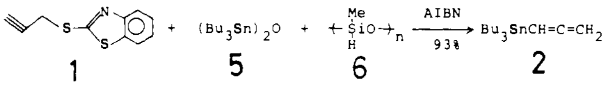
Sir:

The reactions of organotin hydride with double or triple bond normally yield hydrostannylated species, which are useful as synthetic intermediates.[1]

In connection with our work on the desulfurization with organotin compounds,[2] we found an unusual desulfurizative stannylation of propargyl or allyl sulfides with organotin hydride. We report here the first clear-cut example of an S_H' process[3] involving an organotin radical (attacking group) and an organosulfur-centered radical (eliminating group). Thus the tri-*n*-butyltin radical generated from azobisisobutyronitrile (AIBN) and tri-*n*-butyltin hydride[4] (2 equiv) reacted with 2-(propargylthio)benzothiazole (**1**)[5] to give tri-*n*-butylstannylallene (**2**) in 90–93% yield without contamination of propargyltri-*n*-butylstannane (**3**) as shown in the eq 1.[6]



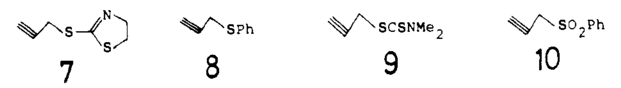
When an equimolar amount of tri-*n*-butyltin hydride was employed, 2-mercaptobenzothiazole (**4**) was isolated in 36% yield in addition to the desired stannylallene (**2**) in 65% yield. Instead of using the isolated tri-*n*-butyltin hydride, the present stannylation reaction was conveniently carried out by the in situ technique[7] using bis(tri-*n*-butyltin) oxide (**5**) and poly(methyl hydrogen siloxane) (**6**).



A typical procedure[8] is as follows. A mixture of bis(tri-*n*-butyltin) oxide (**5**, 2.5 mL, 4.9 mmol) and polysiloxane **6** (0.7 g, 11.6 mmol) was stirred at room temperature for 30 min under argon. Then propargyl sulfide **1** (1.0 g, 4.9 mmol) and catalytic amount of AIBN (10 mg) were added and the resulting mixture was heated at 80–100 °C until the disappearance of the absorptions of acetylene at 3250 and 2100 cm^{-1} and tin hydride at 1800 cm^{-1} (~4–5 h). Stannylallene **2** was isolated by direct distillation from the reaction mixture in 93% yield: bp 80–82 °C (0.15 mmHg); IR (film) 1920 cm^{-1} ($\nu_{CH=C=CH_2}$); NMR ($CDCl_3$) δ 5.0 (t, J = 8 Hz, 1 H, CH=C), 4.16 (d, J = 8 Hz, 2 H, $C=CH_2$), 0.8–1.6 (m, 27 H, Bu_3); *m/e* 330 (M^+), 291, 290, 234, 232, 179, 177, 120, 118, 39.

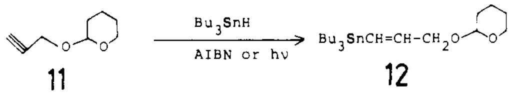
Similar result was obtained with the tri-*n*-butyltin radical generated photolytically. Thus **2** was isolated in 68% yield by irradiation of a degassed benzene (15 mL) solution of **1** (3.9 mmol) and tri-*n*-butyltin hydride (4.9 mmol) with a 100-W high-pressure mercury lamp for 5 h at room temperature in a Pyrex tube.[9]

In order to assess the effect of the organosulfur moiety, we further investigated the several propargyl sulfides (**7**,[10] **8**, **9**) and sulfone **10**.



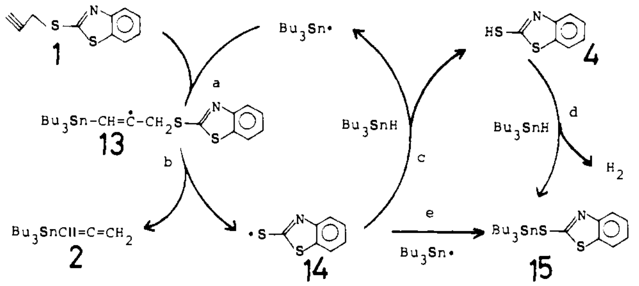
Among these organosulfur compounds, 2-(propargylthio)-1,3-thiazoline (**7**) and propargyl phenyl sulfide (**8**) gave the desired allene (**2**) as main product (>50% yield)[11], while propargyl dithiocarbamate (**9**) and sulfone **10** could not give any allenic products at all under similar conditions at 80–110 °C.[12]

It is quite interesting to note the completely different behavior of propargyl ether toward the tri-*n*-butyltin radical reported by Corey et al.[13] They obtained the normal hydrostannylation product (**12**) in high yield.



The results obtained so far suggest *a principal reaction scheme*, as shown in Scheme I.

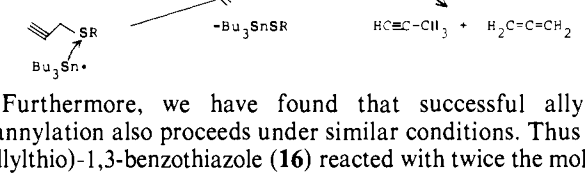
Scheme I



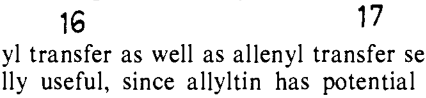
The most important key step is the elimination of the stable sulfur-centered radical such as the benzothiazolythio radical **14** (1,3-thiazolinylthio or phenylthio radical in the case of the compound **7** or **8**, respectively) from the initial adduct such as **13** accompanied with the formation of **2** (step b). The relatively more stable benzothiazolylthio radical **14**[14] in comparison with the other two sulfur radicals seems to give the highest yield of **2** from **1**. On the other hand, in the case of propargyl ether (**11**), the cleavage to the highly unstable alkoxy radical is extremely unfavorable.

Steps c, d, and e are supported by the well-known reaction of the thiyl radical (RS·) with triorganotin hydride.[15] Isolation of **4** in an equimolar reaction also indicates the relatively faster reaction of step c in comparison with step d or e.

Direct homolytic substitution (S_H process) at the sulfur atom is excluded, since such a process should afford a mixture of acetylene and isomeric allene as reported in the case of the reaction of propargyl chloride and tri-*n*-butyltin hydride.[16]



Furthermore, we have found that successful allylic stannylation also proceeds under similar conditions. Thus 2-(allylthio)-1,3-benzothiazole (**16**) reacted with twice the molar amount of tri-*n*-butyltin hydride in the presence of AIBN at 90 °C for 5 h to give tri-*n*-butylallyltin (**17**)[17] in 88% yield: bp 80 °C (0.28 mmHg).



This allyl transfer as well as allenyl transfer seems to be synthetically useful, since allyltin has potential reactivity toward various electrophiles involving σ–π resonance stabilization similar to that of allylsilane.[18]

0002-7863/79/1501-1893$01.00/0

We are currently investigating the present desulfurizative stannylation and its applications to organic synthesis.[19]

References and Notes

(1) R. C. Poller, "The Chemistry of Organotin Compounds", Logos Press, London, England, 1970, pp 105–130.
(2) Y. Ueno, A. Nakayama, and M. Okawara, *J. Am. Chem. Soc.*, **98,** 7440 (1976); for a different approach to the desulfurization of β-halo sulfides with organotin hydride, see T. E. Boothe, J. L. Greene, Jr., and P. B. Shevlin, *ibid.*, **98,** 951 (1976).
(3) Examples of the homolytic substitutions of allylic (or propargyl) compounds via an S_H' process are very few in number; for example, see T. Migita, M. Kosugi, K. Takayanagi, and Y. Nakagawa, *Tetrahedron*, **29,** 51 (1973).
(4) H. G. Kuivila, *Synthesis*, 499 (1970); *Acc. Chem. Res.*, **1,** 299 (1968).
(5) Compound **1** was easily prepared by the reaction of propargyl bromide and 2-mercaptobenzothiazole in the presence of triethylamine (or 2-mercaptobenzothiazole sodium salt) in acetone: mp 45.1–45.6 °C (from EtOH).
(6) The benzothiazole moiety was trapped by tri-*n*-butyltin hydride to produce 2-(tri-*n*-butylstannylthio)benzothiazole (see Scheme I).
(7) G. L. Grady and H. G. Kuivila, *J. Org. Chem.*, **34,** 2014 (1969).
(8) All new compounds obtained here had satisfactory physical and spectral data.
(9) In this case, 2-mercaptobenzothiazole (**4**) was also isolated in 39% yield.
(10) K. Hirai and K. Kishida, *Tetrahedron Lett.*, 2117 (1972).
(11) In this case, the complete separation of stannylallene **2** from the byproducts was difficult by simple distillation.
(12) The structures of the products from dithiocarbamate **9** or sulfone **10** are now under investigation, although the cleavage of sulfone was clearly observed in the case of the compound **10**.
(13) E. J. Corey and R. H. Wollenberg, *J. Org. Chem.*, **40,** 2265 (1975).
(14) J. L. Kice in "Free Radicals", Vol. II, J. K. Kochi, Ed., Wiley, New York, 1973, Chapter 24.
(15) W. P. Newmann and J. Schwindt, *Chem. Ber.*, **108,** 1339, 1346 (1975); e.g., $RS\cdot + R_3'SnH \rightarrow RSH + R_3'Sn\cdot$, $RSH + R_3'SnH \rightarrow RS\text{-}SnR_3' + H_2$.
(16) R. M. Fantazier and M. L. Poutsma, *J. Am. Chem. Soc.*, **90,** 5490 (1968).
(17) Allyltins as well as stannylallenes were hitherto prepared by the Grignard reactions; for example, see M. Kosugi, K. Sasazawa, Y. Shimizu, and T. Migita, *Chem. Lett.*, 301 (1977).
(18) M. Pereyre and J.-C. Pommier in "New Applications of Organometallic Reagents in Organic Synthesis", D. Seyferth, Ed., Elsevier, Amsterdam, 1976, pp 186–187.
(19) In contrast to the propargyl sulfone **10**, allylic sulfones were found to react with tri-*n*-butyltin hydride to produce allyltin compounds via an S_H' process. The details of this allyl transfer will be reported in near future.

Y. Ueno,* M. Okawara
Research Laboratory of Resources Utilization
Tokyo Institute of Technology, Nagatsuta
Midori-ku, Yokohama 227, Japan

Received November 17, 1978

Radical Ions in Photochemistry. 7. Configurational Isomerization of Alkenes Induced by Irradiation of Charge-Transfer Complexes[1]

Sir:

Photophysical studies have firmly established that one of the deactivation pathways of excited charge-transfer complexes and exciplexes can lead to the triplet of either (or both) the component donor or acceptor.[2] This phenomenon is potentially useful for photochemistry since the factors controlling formation of the triplet are not directly dependent upon the decay processes of the individual components of the complex, nor upon the rate of energy transfer as is photosensitization (triplet–triplet transfer). We report here the first example of a configurational isomerization which involves the triplet of an olefin, where the photostationary state is dependent upon the absorption spectra of the charge-transfer complexes involving the individual isomers.

The long-wavelength absorption curves of the donors, *cis*- and *trans*-stilbene (I and II), and the acceptors, maleonitrile (III) and fumaronitrile (IV), and the charge-transfer complexes involving these components, are shown in Figure 1. We call particular attention to differences in the curves for the complexes between *cis*- and *trans*-stilbene and fumaronitrile (Figure 1a). An analysis of the variation in these spectra as a function of fumaronitrile concentration indicates that the difference in these two curves is the result of both a larger association constant and extinction coefficient for the II–IV than for the I–IV complex.[3,4]

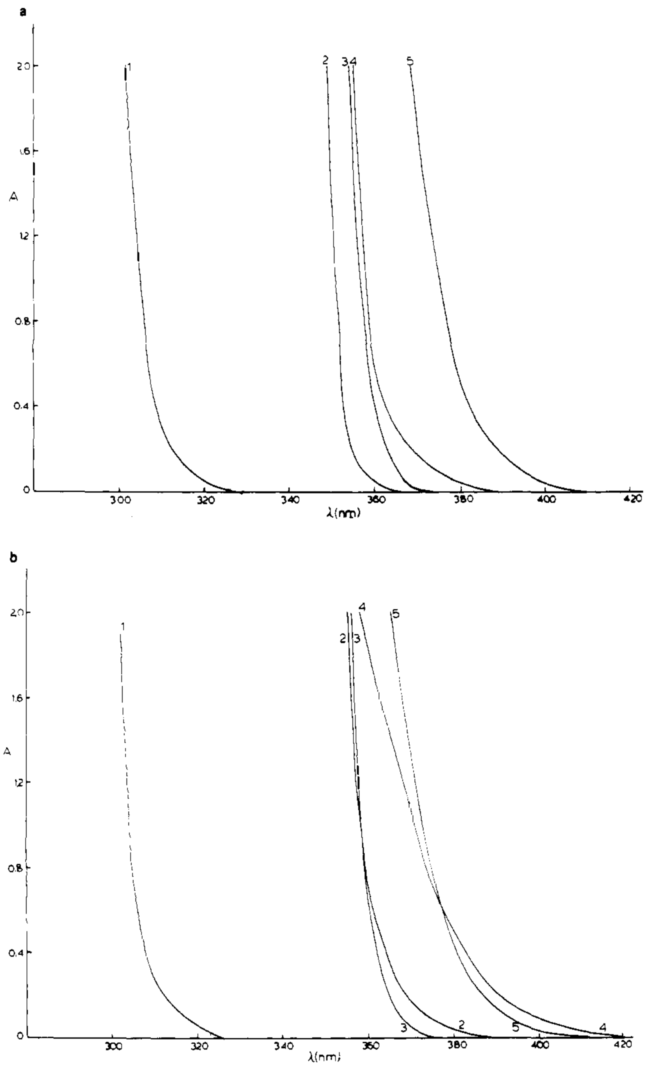


Figure 1. a, (1) 0.2 M IV, (2) 0.2 M II, (3) 0.2 M I, (4) 0.2 M I + 0.2 M IV, (5) 0.2 M II + 0.2 M IV (benzene solution); b, (1) 0.2 M III, (2) 0.2 M I + 0.2 M III, (3) filter solution A, 1 cm (1 g of $BiCl_3$ in 150 mL of 10% HCl), (4) Corning glass filter 0-51, (5) 0.2 M II + 0.2 M III (benzene solution).

Irradiation of a degassed benzene solution of *trans*-stilbene (II, 0.2 M) and fumaronitrile (IV, 0.2 M) in the region of the charge-transfer transition (λ >356 nm) leads predominantly to isomerization of both the stilbene and the dinitrile; other photochemical reactions are relatively unimportant. The progress of the isomerizations can be followed by vapor-phase chromatography (VPC) and ^1H nuclear magnetic resonance (NMR) spectroscopy and the isomeric compositions, as a function of irradiation time, are summarized in Table I.

The isomerization of the *trans*-stilbene is more efficient than that of the dinitrile and the mixture attains a maximum (>80%) composition of *cis*-stilbene. Continued irradiation leads to a decrease in the *cis*- to *trans*-stilbene ratio as the fumaronitrile isomerizes to maleonitrile. Prolonged irradiation (10 days) gives the photostationary state, which is also obtained starting with I and IV. An even higher ratio (I/II, 6) of *cis*-stilbene can be attained if a light filter which cuts off irradiation of longer wavelengths (λ >360 nm) is used, although the isomerization is much slower since less light is absorbed under these conditions. Notice, in Figure 1a, that both I and II absorb beyond the cut-off of filter A (λ >356 nm). Prolonged irradiation of II under these conditions causes isomerization to a

0002-7863/79/1501-1894$01.00/0