Excellent stereochemical control is exerted in all cases, except for 3-sulfolene. Furthermore removal of the chiral auxiliary did not lead to racemization. In fact in all cases studied so far (except for entry 6) only one diastereoisomer of the Diels–Alder product was found when enantiomerically pure **3a** was used as dienophile. With anthracene even at 190 °C in decalin as a solvent the same stereoselectivity was observed. Preliminary experiments showed that the reaction of **3a** and anthracene can also be performed at 20 °C by using $TiCl_4$ as Lewis acid catalyst with a de >96%.

In conclusion, we have demonstrated that preparative easily accessible (menthyloxy)butyrolactones can be effectively used in new asymmetric Diels–Alder reactions with cyclic and acyclic dienes to give virtually enantiomerically pure Diels–Alder products. No Lewis acid catalysis is required, and the chiral auxiliary can be recovered by mild procedures. Furthermore both enantiomers of the chiral auxiliary are readily available. Applications of this methodology in natural product synthesis is currently under investigation.

Acknowledgment. Use of the services and facilities of the Dutch CAOS/CAMM Center, under Grants SON-11-20-700 and STW-NCH-44.0703, is gratefully acknowledged.

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[15] The capillary GC column used was a XE-60 (*S*)-valine-(*S*)-α-phenylethylamine (50 m × 0.25 mm, Chrompack). Racemic methoxy adducts gave two well-separated peaks for the enantiomers, whereas a single peak was observed for enantiomerically pure products when using this column.

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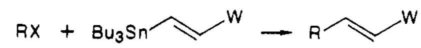
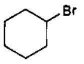
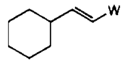
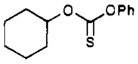
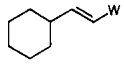
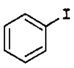
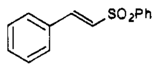
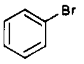
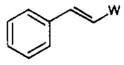
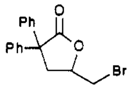
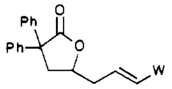
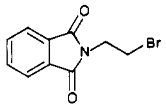
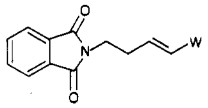
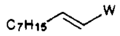
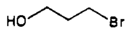
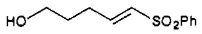
A Free Radical Addition–Fragmentation Reaction for the Preparation of Vinyl Sulfones and Phosphine Oxides

Summary: A free radical chain process is reported which gives vinyl sulfones or phosphine oxides in good to moderate yields under nonreducing conditions; the reaction involves irradiation of appropriate precursors to carbon-centered radicals with β-tri-*n*-butylstannyl α,β-unsaturated sulfones or phosphine oxides in the presence of AIBN.

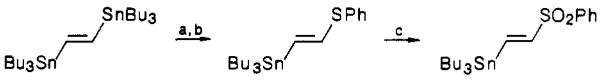
Sir: The development of free radical or "one-electron" chain processes for the formation of C–C bonds has been an area of ongoing interest.[1] While our previous efforts in this area have focused on the general process of free radical allylation, utilizing allylic stannanes[2] and sulfides,[3] we have also been interested in the development of reagents for free radical vinylation reactions. Specifically, we hoped to design simple reagents which could deliver a vinyl synthon to carbon-centered radicals under nonreducing radical conditions.[4]

Table I. Isolated Yields for Vinyl Sulfones and Phosphine Oxides



substrate	product	yield (reagent, product E/Z Ratio)
		79% (W = SO_2Ph) 61% (W = $PO(Ph)_2$)
		83% (W = SO_2Ph) 75% (12:1, W = $PO(Ph)_2$)
		82% (8:1)
		45% (6:1, W = SO_2Ph) 42% (6:1, W = $PO(Ph)_2$)
		73% (W = SO_2Ph) 46% (8:1, W = $PO(Ph)_2$)
		77% (W = SO_2Ph) 58% (10:1, W = $PO(Ph)_2$)
$C_7H_{15}I$		76% (W = SO_2Ph) 78% (8:1, W = $PO(Ph)_2$)
		66%

One such reagent that we have examined is 1-(tri-*n*-butylstannyl)-2-(phenylsulfonyl)ethene (**1**). This reagent is prepared in two operations and 79% overall yield from (*E*)-1,2-bis(tri-*n*-butylstannyl)ethene[5] (**2**) as shown in eq 1.



(1)

2 **3** **4**

(a) 1.1 equiv of *n*-BuLi, THF, −78 °C; (b) PhSSPh, −78 to −25 °C; (c) 2.2 equiv of *m*-CPBA, CH_2Cl_2, −45 to −25 °C.

Photolysis[7] of a variety of alkyl and aryl iodides, bromides, and phenylthionocarbonates with an excess of **1** and catalytic AIBN in benzene led to the formation of vinyl sulfones in usually good yields as shown in Table I.[8] The predominant isomer in all cases examined is of the *E*

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[1] For a recent and very readable account of radical reactions in organic synthesis, note: Hart, D. J. *Science (Washington, D.C.)* **1984**, *234*, 883. A recent symposium-in-print has been devoted to radical reactions and contains many relevant articles: Giese, B., Ed. *Tetrahedron* **1985**, *41*, 3887.

[2] (a) Keck, G. E.; Yates, J. B. *J. Am. Chem. Soc.* **1982**, *104*, 5829. (b) Keck, G. E.; Enholm, E. J.; Yates, J. B.; Wiley, M. W. *Tetrahedron* **1985**, *41*, 4079.

[3] Keck, G. E.; Byers, J. H. *J. Org. Chem.* **1985**, *50*, 5442.

[4] The term "nonreducing conditions" means that the radical chain is terminated by some means other than hydrogen abstraction by the product.

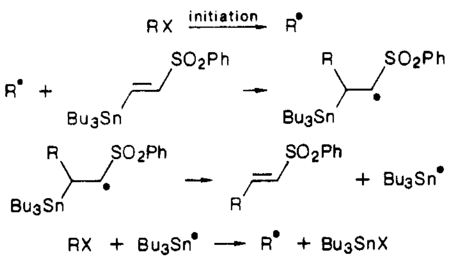
[5] (a) Corey, E. J.; Wollenberg, R. H. *J. Org. Chem.* **1975**, *40*, 3788. (b) The monolithiation and quenching of **2** with a variety of electrophiles is discussed in: Wollenberg, R. H. Ph.D. Thesis, Harvard University, 1976.

[6] Attempts to prepare **1** more directly, by quenching the vinyllithium prepared from **2** with benzenesulfonyl chloride, led to extensive polymerization.

[7] The light source for photolysis was a 450-W Hanovia lamp equipped with a Pyrex filter.

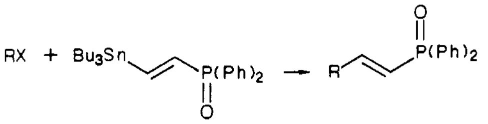
[8] A general procedure for all reactions is as follows. In a screw-top Pyrex test tube were placed 0.33 mmol of the substrate, 1 mmol of **1** which had been freshly flushed through a pad of alumina, 0.03 mmol of AIBN, and 1 mL of benzene. The solution was degassed by bubbling argon through the reaction mixture for ~15 min, and the tube was secured adjacent to the photolysis lamp. Photolysis for 12 h was usually sufficient for the completion of the reaction, except when aryl halides were employed as substrates, in which case the reaction took a greater length of time. When the reaction was complete, as indicated by the disappearance of the substrate by TLC or GC, the crude mixture was diluted to 25 mL with ether, washed with 10 mL saturated KF solution, and purified by medium-pressure liquid chromatography. The unreacted excess of **1** could usually be recovered during chromatography and reused in subsequent experiments.

Scheme I



configuration, based upon the coupling constants observed for the olefinic hydrogens. The E/Z ratios were obtained where possible by NMR integration or were otherwise obtained by analytical HPLC. In cases where no ratio is listed, none of the Z isomer was detected or identified.[9]

A parallel process can also be used for the preparation of α,β-unsaturated phosphine oxides. Thus, treatment of **2** with n-butyllithium followed by addition of diphenylphosphinic chloride gives the requisite reagent **4**, albeit in moderate (43%) isolated yield. Reaction of this reagent with various precursors to carbon centered radicals then yields predominately trans α,β-unsaturated phosphine oxides as shown in eq 2 and Table I. Yields are generally not as high with this reagent as with reagent **1**.



4

(2)

A mechanistic rationale for these radical chain processes is outlined in Scheme I for the case of the phenylsulfonyl reagent **1**.

The carbon centered radical, R•, presumably attacks C_1 of the vinylation reagent to generate the α-phenylsulfonyl radical. This radical intermediate can then undergo β-scission to form the vinylated product and the tri-n-butylstannyl radical, which in turn propagates the chain process.[10] It is important to note that reactions of this type do not appear to proceed without some functional group stabilization of the intermediate radical. For example, upon attempted reaction of vinyltri-n-butylstannane with a variety of carbon-centered radicals, none of the desired vinylated product could be obtained. In addition, all attempts to utilize reagent **2** in such reactions were also unsuccessful.

The vinyl sulfone moiety has been shown by others to be a valuable and versatile functional array for further synthetic transformations.[11] In particular, in the context of free radical "vinylation", such aryl vinyl sulfones are known to undergo reductive desulfonylation with sodium amalgam to yield the corresponding vinyl compounds.[12] Further studies involving net free radical vinylations by such addition–fragmentation strategies are under way at the present time.[13]

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[9] The Z isomer was obtained only in those cases where R of the substrate RX was aromatic. An observed time dependence of the E/Z ratio suggests light-induced isomerization of Z to E substituted styrenes as the origin of Z products in these cases.

[10] Mechanistically similar radical addition–fragmentation processes involving radical addition to electron deficient olefins have been recently described: (a) Baldwin, J. E.; Kelly, D. R.; Ziegler, C. B. *J. Chem. Soc., Chem. Commun.* **1984**, 133. (b) Russell, G. A.; Tashtoush, H.; Ngoviwatchai, P. *J. Am. Chem. Soc.* **1984**, *106*, 4622. (c) Keck, G. E.; Burnett, D. A. *J. Org. Chem.* **1987**, *52*, 2958.

[11] Some recent examples of the use of vinyl sulfones in organic synthesis: (a) Cory, R. M.; Renneboog, R. M. *J. Org. Chem.* **1984**, *49*, 3898. (b) Hamann, P. R.; Toth, J. E.; Fuchs, P. L. *J. Org. Chem.* **1984**, *49*, 3865. (c) Carr, R. V. C.; Williams, R. V.; Paquette, L. A. *J. Org. Chem* **1983**, *48*, 4976. (d) Kinney, W. A.; Crouse, G. D.; Paquette, L. A. *J. Org. Chem.* **1983**, *48*, 4986. (e) Hamann, P. R.; Fuchs, P. L. *J. Org. Chem.* **1983**, *48*, 914. (f) Fabre, J. L.; Julia, M.; Verpeaux, J. N. *Tetrahedron Lett.* **1982**, 2469. (g) Bremmer, J.; Julia, M.; Launay, M.; Stacino, J. P. *Tetrahedron Lett.* **1982**, 3265. (h) Agawa, T.; Yoshida, Y.; Komatsu, M.; Oshiro, Y. *J. Chem. Soc., Perkin Trans. 1* **1981**, 75. (i) Review: Julia, M.; Uguen, D.; Righini, A.; Launay, M.; Verpeaux, J. N. *Int. Congr. Ser.—Excerpta Med.* **1979**, *457*, 163.

[12] (a) Davis, A. P.; Whitham, G. H. *J. Chem. Soc., Chem. Commun.* **1980**, 639. (b) Trost, B. M.; Arndt, H. C.; Strege, P. E.; Verhoeven, T. R. *Tetrahedron Lett.* **1976**, 3857.

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