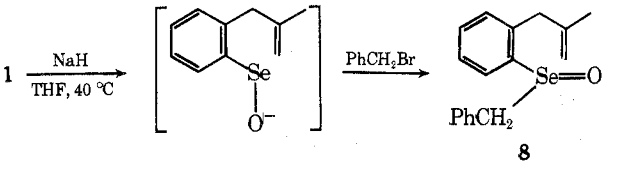
reaction of selenoxides compared with that of sulfoxides is reasonably accounted for by the 4–5 pK_a greater basicity of selenoxides.[12] The spectroscopic and analytic properties of **7** are fully compatible with the proposed structure and with the data obtained for analogous sulfur and phosphorus ylides. In particular, the *gem*-dimethyls are diastereotopic and show $^{77}Se–H$ and $^{77}Se–^{13}C$ coupling in the proton and carbon NMR spectra,[13] proving that geometry at selenium is pyramidal, and that the five-membered ring is intact.

Decomposition of **1** in the presence of a strong base and an alkylating agent such as benzyl bromide results in the formation of benzyl selenoxide **8**, presumably by Se alkylation of the selenenate ion.[14] This result suggests that the transformation of halides or sulfonates to olefins could be carried out by a selenenate alkylation–selenoxide elimination sequence, perhaps even in a catalytic fashion.



Only a few selenenic acids with special substitution have been isolated and characterized.[15] The results reported here, together with previous studies of selenenamide chemistry,[6] point to the emergence of significant differences between selenenic acids and their sulfur analogues.

Acknowledgment. The donors of the Petroleum Research Fund, administered by the American Chemical Society, provided support for this work. We thank David Ting for technical assistance.

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(5) Proton NMR: 1.13 (t, $J = 7$ Hz, 6 H), 1.69 (s, 3 H), 3.08 (q, $J = 7$ Hz, 4 H), 3.28 (s, 2 H), 4.59 (br s, 1 H), 4.80 (br s, 1 H), 7.08 (m, 3 H), 7.75 (m, 1 H). Carbon NMR: 14.26, 54.11 (NEt), 22.46 (CH_3), 43.22 (CH_2), 112.73 (CH_2═C), 125.80, 126.59, 128.08, 129.73, 137.03 (q), 137.18 (q), 143.64 (q) (aryl, vinyl C).
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(12) The pK_a of selenolane oxide is 3.3 (H. J. Reich, J. E. Trend, unpublished results). The pK_a of thiolane oxide is −1.34 [R. Curci, F. DiFuria, A. Levi, V. Lucchini, and G. Scorrano, *J. Chem. Soc., Perkin Trans. 2*, 341 (1975)].
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(16) Alfred P. Sloan Fellow, 1975–1977.

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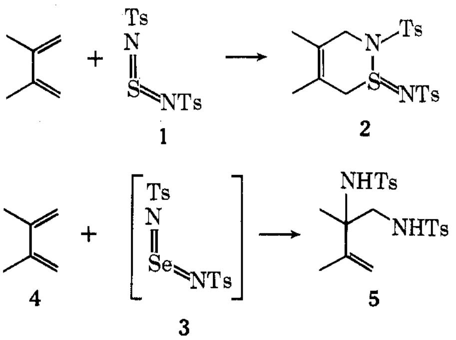
Received April 2, 1976

1,2-Diamination of 1,3-Dienes by Imido Selenium Compounds

Summary: Solutions thought to contain the selenium diimide species **3** (TsN═Se═NTs) react with 1,3-dienes to produce 1,2-disulfonamides. In the case of 1,3-cyclohexadiene the sulfonamide groups are introduced cis to each other.

Sir: We have reported that aza analogues (**1** and **3**) of both selenium dioxide[1] and sulfur dioxide[2,3] effect allylic amination of olefins. Since it is well known that the imides of sulfur dioxide (e.g., **1**) readily undergo cycloadditions with dienes to produce stable [4 + 2] adducts (e.g., **2**),[4] we attempted to trap the putative selenodiimide intermediate **3** as its [4 + 2] adduct with 2,3-dimethylbutadiene (**4**). However, only the vicinal disulfonamide **5** could be isolated. This reaction was found to occur with a variety of 1,3-dienes (Table I), and is envisioned as proceeding through the pathway shown in Scheme I for 1,3-cyclohexadiene (**6**). In support of this pathway, hydrogenation (PtO_2, 5 psi H_2 pressure, EtOAc) of the product, disulfonamide **7**,[5a] gave only *cis*-1,2-di(*p*-toluenesulfonamido)cyclohexane.[5b] Exclusive cis stereochemistry



Scheme I

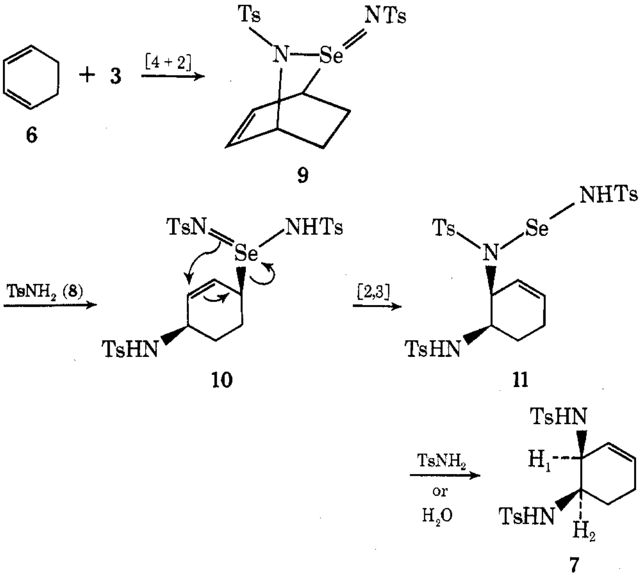
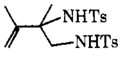
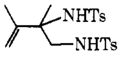
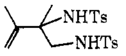
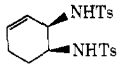
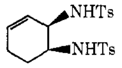
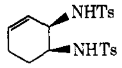
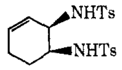
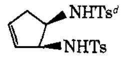
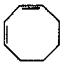
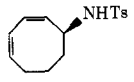
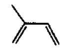
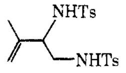
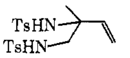
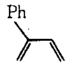
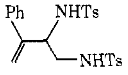
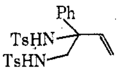
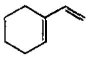
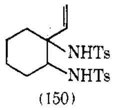
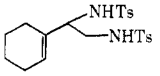


Table I. 1,2-Diamination of 1,3-Dienes[a]

Case	Diene	Equiv of 3	Equiv of $TsNH_2$ (10)	Products[b]	% yield[c]
1		1.1	1.1	 (136)	68
2		1.1	0	 (136)	4
3		2.5	0	 (136)	61
4		3.75	3.75	 (158-159)	37
5		1.25	1.25	 (158-159)	29
6		2.5	0	 (158-159)	15
7		1.1	0	 (158-159)	0
8		1.1	1.1	 (142.5)	40
9		1.1	1.1	 12 (113.5)	52
10		1.1	1.1	 (144-145)	26
					8
11		1.1	1.1	 (157)	45
					8
12		1.1	1.1	 (150)	37
					4

[a] All reactions were run on a 10-mmol scale as described in the general procedure. [b] The melting point (°C) appears in parentheses below the structure. [c] In the case of solid products the yields are for recrystallized substances. When no melting point is given, the substance was an oil, and the yield is for chromatographically pure material. [d] The stereochemistry is assumed to be cis by analogy with the 1,3-cyclohexadiene case.

is expected in cyclic systems since all steps must occur on the same face of the molecule. Addition of an equivalent of *p*-toluenesulfonamide (**8**) during reagent generation resulted in greatly improved yields of the 1,2-disulfonamides (e.g., cases 1 and 2 in Table I). The *p*-toluenesulfonamide is presumed to effect cleavage of the seleninolactam **9** to the intermediate **10**, which is then able to undergo [2,3] rearrangement[6] leading, via selenium(II) amide **11**, to the observed products. In the absence of nucleophiles such as sulfonamide **8**, lactam **9** seems to decompose to a variety of selenium containing compounds. The reagent **3** is generated from anhydrous Chloramine-T which probably always contains traces of *p*-toluenesulfonamide. This would account for the formation of some vicinal diamide even when sulfonamide is not intentionally added (cases 2, 3, 6, and 7 of Table I).

A seleninolactone analogous to lactam intermediates of type **9** was isolated by Mock upon reaction of dimethylbutadiene **4** with selenium dioxide.[7,8] It seemed likely that under aqueous conditions such lactones should undergo hydrolysis and [2,3] rearrangement to 1,2-diol products in a manner analogous to that proposed for formation of the 1,2-disulfonamides (**7**) in Scheme I. In support of this reasoning, reaction of cyclohexadiene **6** with 1 equiv of selenium dioxide in aqueous *tert*-butyl alcohol gave *cis*-3,4-dihydroxycyclohexene[9] (22% yield) as the only nonselenium containing organic product.

Even though no diene remains after a few hours, examination of Table I reveals that the yields of disulfonamide are generally only poor to fair. Polar, uncharacterized by-products were formed in most cases; however, these were easily removed by chromatography on alumina. Interestingly, 1,3-cyclooctadiene (case 9) gave the allylic sulfonamide **12** as the only isolated product; in this instance the ene reaction[1] takes precedence over the [4 + 2] cycloaddition.[10]

General Procedure. A silver-gray slurry of the reagent was prepared by stirring a mixture of 1.08 g (13.6 mg-atoms) of powdered selenium metal, 5.69 g (25 mmol) of anhydrous[11] Chloramine-T, and 2.14 g (12.5 mmol) of dry[11] *p*-toluenesulfonamide in 50 ml of dry[11] methylene chloride under nitrogen for 15 h at room temperature.[12] The diene (10 mmol) was added and stirring was continued overnight. Water (20 ml) was added and, after stirring for 15 min, the dark reaction mixture was poured into 100 ml of 1:1 ethyl acetate/ether and 100 ml of 1:1 4% NaOH/brine. After filtering through Celite, the organic phase was washed twice with 1:1 4% NaOH/brine to remove the residual sulfonamide, then once with brine, and finally was dried ($MgSO_4$) and concentrated to afford the crude product. The products were isolated by chromatography on 250 g of activity III (6% H_2O) basic alumina using hexane/EtOAc mixtures as eluent. The products were recrystallized from either $CHCl_3$/hexane or acetone/hexane. All new compounds gave consistent analytical and spectral data.

Acknowledgment. We thank the National Institutes of Health (GM21686) for support of this research and our colleagues R. V. Punzar and D. S. Kemp for samples of *cis*- and *trans*-1,2-diaminocyclohexane.

References and Notes

(1) K. B. Sharpless, T. Hori, L. K. Truesdale, and C. O. Dietrich, *J. Am. Chem. Soc.*, **98**, 269 (1976).
(2) K. B. Sharpless and T. Hori, *J. Org. Chem.*, **41**, 176 (1976).
(3) Kresze has also recently reported the ene reaction of sulfur diimides with olefins [N. Schönberger and G. Kresze, *Justus Liebigs Ann. Chem.*, 1725 (1975)].
(4) G. Kresze and W. Wucherpfennig, *Angew. Chem., Int. Ed. Engl.*, **6**, 149 (1967).
(5) (a) Results from NMR decoupling experiments are consistent with the proposed cis relationship between the sulfonamide groups in **7** ($J_{1,2}$ = 4 Hz in $CDCl_3$ containing 0.1 N $NaOD/D_2O$). (b) Its identity was established by comparison with an authentic sample prepared by reaction of *cis*-1,2-diaminocyclohexane [A. I. Smith, U.S. Patent 3 167 586 (1965)] with excess *p*-toluenesulfonyl chloride in pyridine.
(6) A [2,3]rearrangement of the corresponding sulfur(IV) species is described in ref 2.
(7) W. L. Mock and J. H. McCausland, *Tetrahedron Lett.*, 391 (1968).
(8) Other similar seleninolactones have been isolated recently [D. Arigoni, A. Vasella, K. B. Sharpless, and H. P. Jensen, *J. Am. Chem. Soc.*, **95**, 7917 (1973)].
(9) H. Z. Sable et al., *Tetrahedron*, **26**, 1509 (1970).
the dienophile [O. L. Chapman and S. J. Dominianni, *J. Org. Chem.*, **31**, 3862 (1966)].
(11) Anhydrous Chloramine-T is available from Aldrich (see also ref 1). The *p*-toluenesulfonamide was dried at 80° under high vacuum for 12 hr. The methylene chloride was passed through neutral activity I alumina and stored over 4Å molecular sieves.
(12) At this time, the exact nature of the reactive species present in the slurry in not known. However, this reagent, formed in the presence of an equivalent of $TsNH_2$, is different from the reagent (ref 1) formed in the absence of sulfonamide. It seems to form more rapidly, and the resulting suspension

has a silver-gray luster. When cyclohexene was treated with 1.25 equiv of this new reagent, the allylic sulfonamide was obtained in somewhat improved yield (~10% better than using 1.25 equiv of the reagent in ref 1). However, when only 0.63 equiv of this new reagent was employed, it gave the same yield of allylic amide as did 0.63 equiv of the original reagent (ref 1). Further comparisons are needed, but it appears that this modified reagent may also be useful for the allylic aminations of olefins.

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Received February 18, 1976

Preparative Methods for β-Acyl Vinyl Anion Equivalents from Enones or Allyl Sulfides

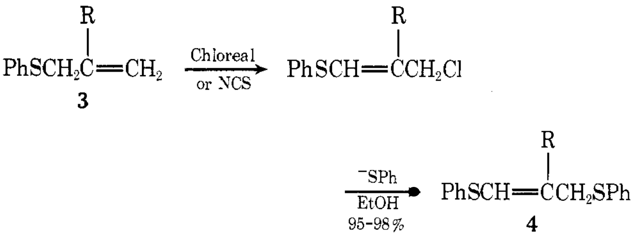
Summary: The treatment of many α,β-unsaturated aldehydes and ketones with triphenyl thioborate provides the 1,3-bis(phenylthio)alkene derivatives, the anions of which are shown to be effective β-acyl vinyl anion equivalents.

Sir: We wish to report that a variety of α,β-unsaturated aldehydes and ketones (1) can be converted directly to their 1,3-bis(phenylthio)alkene derivatives (2) by heating in hydrocarbon solvents with triphenyl thioborate (eq 1);[1] this reagent is readily prepared from B_2S_3 and thiophenol.[4] Several examples are given in Table I.

$$\underset{\mathbf{1}}{\mathrm{R_2CH{=}C(R_1)COR_3}} \xrightarrow{\mathrm{B(SPh)_3}} \underset{\mathbf{2}}{\mathrm{PhSCH(R_2)C(R_1){=}C(SPh)R_3}} \qquad (1)$$

This simple reaction gives a poor yield with acrolein and fails completely with methyl vinyl ketone.[5] Fortunately, the desired products from both reactions can be prepared by alternative routes. That (**4**, R = H) from acrolein can be prepared from phenyl allyl sulfide (**3**, R = H; commercially available) by the sequence in Scheme I; as pointed out elsewhere,[6] the chlorination is faster with the far less expensive reagent trichloroisocyanuric acid (Chloreal), but *N*-chlorosuccinimide can be used.[7] The bis(phenylthio) derivative (**4**, R = Me) of methacrolein can be prepared in a similar fashion; this sequence has been performed on a 20-g scale. The product **7**, expected from methyl vinyl ketone (**5**), can be prepared from the latter by treatment with thiophenol and HCl, followed by elimination of thiophenol from the condensation product (**6**) by cuprous trifluoromethanesulfonate (triflate)[8] (Scheme II).[9]

Scheme I



Scheme II

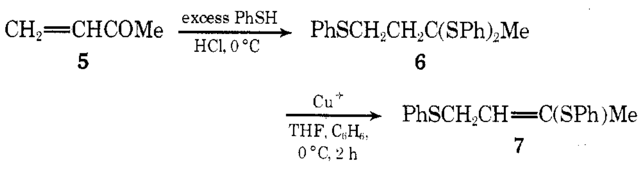


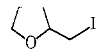
Table I. Reactions of Enones with Triphenyl Thioborate[a]

R_1[b]	R_2[b]	R_3[b]	% yield of **8**[c]
H	$CH_2CH_2CH_2$		78
H	CH_2CH_2		43
$CH_2CH_2CH_2CH_2$		Me	50[d,e]
H	Me	H	66[f]
Me	H	H	70[g]
H	H	H	35
H	H	Me	[h]

[a] Satisfactory spectral and elemental analyses were obtained on all new compounds. [b] Refers to eq 1. [c] In a typical run, 9.3 mmol of **1** was heated with 6.2 mmol of $B(SPh)_3$ at 50 °C in petroleum ether (60–110 °C) for 15 h; removal of the precipitate by filtration and evaporation of the solvent provide the isolated yields recorded. [d] Reaction performed at 150 °C for 24 h in a sealed tube; no product was obtained at 50 °C. [e] Cis–trans mixture. [f] 75% trans. [g] 50% trans. [h] Only 4-phenylthio-2-butanone produced.

Table II. Reactions of Bis(phenylthio)allyl Anions with Alkyl Halides[a]

$$\mathrm{PhSCH(R_2)C(R_1){=}C(SPh)R_3} \xrightarrow[\text{2. RX}]{\text{1. } sec\text{-BuLi, THF, } -20\ ^\circ\text{C, 45 min}} \mathrm{PhSC(R_2)(R)CR_1{=}C(SPh)R_3}$$

R_1	R_2	R_3	RX	% yield
H	H	H	MeI	98
H	H	H	*i*-BuI	98
Me	H	H	MeI	94
Me	H	H	*n*-BuI	98
Me	H	H		94
H	$CH_2CH_2CH_2$[b]		MeI	90
H	Me[b]	H	MeI	98[c]
H	H	Me	MeI	98[c]

See footnote *a*, Table I. [b] When R_2 is alkyl, HMPA must be present to generate the anion quantitatively. [c] 90% methylation at secondary carbon, 10% at tertiary.

These bis(phenylthio)alkenes have many potential uses but one of the most important derives from the behavior of their lithio derivatives as β-acyl vinyl anion equivalents.[10] The results in Table II indicate that the lithio derivatives can be formed readily and alkylated efficiently. The anion of **8**, derived from cyclohexenone, also added to benzaldehyde and underwent conjugate addition to chalcone in 90 and 95% yields, respectively.

The otherwise unfunctionalized 1,3-bis(phenylthio)alkenes can be hydrolyzed to enones by mercuric chloride in wet acetonitrile as found by Corey[10] for the methylthio analogues; this was demonstrated for **2** (R_1 = Me, R_2 = *n*-butyl, R_3 = H)[11] and **9**. The ketone **10**, however, gave only a 25% yield of enone and a large quantity of insoluble material by this method. The following procedure, based on our new method of carbonium ion formation,[8] is successful for both **10** and **8**;[13] a solution of 0.20 mmol of **10** and 0.40 mmol of the benzene complex of cuprous triflate in 5 ml of acetonitrile and 0.5 ml of water[14] was heated at reflux for 10 h, cooled, and passed rapidly through a silica column and the solvent evaporated.

Thus, for example, the overall transformations shown in Scheme III have been realized.

It is clear that these techniques will frequently allow the replacement of a β hydrogen of a conjugated enone by an electrophilic substituent.[15] However, as implied by the last two entries in Table II (Scheme IV), in the case of enones