to the method of Markgraf and Katt[10] by potentiometric titration with a Radiometer RTS622 Recording Titration System fitted with a glass indicator electrode and a saturated calomel reference electrode, previously equilibrated with acetic anhydride for 48 h. Titrations were carried out at 25.00 ± 0.05 °C under a nitrogen atmosphere in a water-jacketed cell connected to a constant temperature bath and fitted with a neoprene cover drilled to accommodate two electrodes, a buret, thermometer, and nitrogen inlet tube. In a typical run, an accurately weighed amount of the pyridine derivative (ca. 5×10^{-4} mol) was dissolved in acetic anhydride in a nitrogen-swept 25-mL volumetric flask; a 10-mL aliquot was transferred to the titration cell, diluted with 60 mL of acetic anhydride, and with magnetic stirring titrated with 0.10 N perchloric acid in acetic acid (Fisher No. SO-P-339, ca. 3.5 mL). The end point and half-neutralization potential were determined graphically. All runs were carried out in duplicate, with a precision of ±2 mV.

Acknowledgment. Financial support from the Robert A. Welch Foundation is gratefully acknowledged. The Varian XL-100 NMR spectrometer was obtained with a major equipment grant from the National Science Foundation.

Registry No.—1, 56911-25-2; 2, 56911-27-4; 3, 533-37-9; 4, 10500-57-9; 5, 533-35-7; 6, 36556-06-6; 10, 278-33-1; 11, 327-60-6; propargyl 4-pyridyl ether *N*-oxide, 67858-39-3; propargyl 4-pyridyl ether, 64818-18-4; proparyl alcohol, 107-19-7; 4-nitropyridine *N*-oxide, 1124-33-0.

References and Notes

(1) R. P. Thummel and D. K. Kohli, *J. Org. Chem.*, **42**, 2742 (1977).
(2) J. M. Riemann and W. S. Trahanovsky, *Tetrahedron Lett.*, 1867 (1977).
(3) W. D. Crow, A. N. Khan, and M. N. Paddon-Row, *Aust. J. Chem.*, **28**, 1741 (1975).
(4) R. P. Thummel and W. Nutakul, *J. Org. Chem.*, **43**, 3170 (1978).
(5) (a) C. A. Streuli, *Anal. Chem.*, **30**, 997 (1958); (b) V. K. Kondratov and E. G. Novikov, *Russ. J. Phys. Chem.* (*Engl. Transl.*), **45**, 1259 (1971); *Chem. Abstr.*, **75**, 151248m (1971).
(6) A. Streitweiser, Jr., G. R. Ziegler, P. C. Mowry, A. Lewis, and R. G. Lawler, *J. Am. Chem. Soc.*, **90**, 1357 (1968); see also R. A. Finnegan, *J. Org. Chem.*, **30**, 1333 (1965).
(7) W. Adcock, B.D. Gupta, T. C. Khor, D. Doddrell, and W. Kitching, *J. Org. Chem.*, **41**, 751 (1976).
(8) (a) E. R. Lavagnino, R. R. Chauvette, W. N. Cannon, and E. C. Kornfield, *J. Am. Chem. Soc.*, **82**, 2609 (1960); (b) D. S. Wulfman and T. R. Steinheimer, *Tetrahedron Lett.*, 3933 (1972).
(9) (a) J. M. Riemann and W. S. Trahanovsky, *Tetrahedron Lett.*, 1863 (1977), footnote 2; (b) W. S. Trahanovsky, C. C. Ong, J. G. Pataky, F. L. Weitl, P. W. Mullen, J. C. Clardy, and R. S. Hansen, *J. Org. Chem.*, **36**, 3575 (1971).
(10) J. H. Markgraf and R. J. Katt, *J. Org. Chem.*, **37**, 717 (1972).

Ramberg–Backlund Sulfur Extrusion from 2-Carboethoxy Sulfones

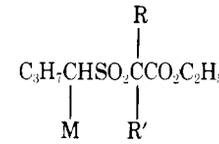
Edwin Vedejs* and Stephen P. Singer

Chemistry Department, University of Wisconsin, Madison, Wisconsin 53706

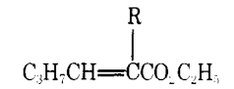
Received February 14, 1978

Previous studies in our laboratory have established an efficient ring expansion route to 2-carboethoxythiacycloalkenes of variable ring size.[1] In this note, we describe a simple procedure for conversion of the ring expansion products into carbocycles by Ramberg–Backlund sulfur extrusion. The method employs the convenient chlorinating agent hexachloroethane,[2] which is compatible with NaH or $KOC(CH_3)_3$ and can be used in a one-pot Ramberg–Backlund process.

In a simple example of the one-pot reaction, the α-methyl sulfone ester **1** reacts with excess NaH and 1.2 mol of C_2Cl_6 (DME solution, 20 °C) to give ethyl 2-methylhex-2-enoate (**2**) in 54% isolated yield (1:1 *E*/*Z*). Similar treatment of the unsubstituted sulfone ester **3** affords an α-chloro derivative **4** (60% isolated, not optimized), but **4** does not undergo Ramberg–Backlund sulfur extrusion upon treatment with various bases. This observation suggests that **4** is converted into the enolate **5**, which is strongly favored relative to **6**, the anion required for episulfone formation. In the absence of an enolizable hydrogen, eipsulfone formation can occur. Thus, treatment of **4** with excess C_2Cl_6 and sodium hydride results in slow formation of ethyl 2-chlorohex-2-enoate (**7**) (*E*,*Z* mixture) via α-dichloro sulfone ester **8**.



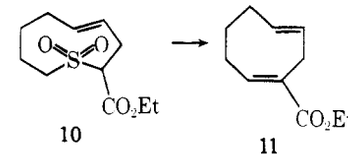
1, R = CH_3; R′ = M = H
3, R = R′ = M = H
4, R = Cl; R′ = M = H
5, R = Cl; R′ = Li; M = H
6, R = Cl; R′ = H; M = Li
8, R = R′ = Cl; M = H
9, R = CH_3; R′ = Cl; M = H



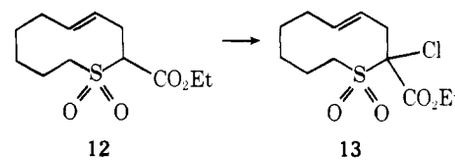
2, R = CH_3
7, R = Cl

The one-pot Ramberg–Backlund conditions described above have been optimized for sulfur extrusion from the nine-membered sulfone ester **10**. After 3 h at 20 °C, the novel *cis,trans*-cyclooctadiene ester **11** can be isolated in 75% yield by distillation of the crude product. In support of structure **11**, the NMR spectrum shows two hydrogens of a disubstituted trans double bond (J_{vinyl} = 16 Hz), the β proton of an unsaturated ester (6.7 ppm), and a doubly allylic methylene ABX pattern centered at 3.0 ppm. A characteristic *trans*-cyclooctene infrared band at 985 cm^{-1} is further evidence for structure **11**. Analogous sulfur extrusion from the ten-membered ring **12** is considerably slower. After 24 h at 20 °C, 33% of the cyclononadiene **14** (IR 988 cm^{-1}; NMR 6.96 ppm, unsaturated ester β-H) was isolated, together with 54% of α-chloro sulfone **13**. Prolonged reaction with sodium hydride favors **14** at the expense of **13**. Starting with purified **13**, a more rapid conversion can be achieved with potassium *tert*-butoxide and gives a 50% isolated yield of **14**.

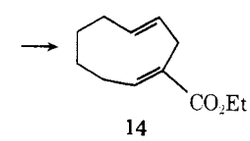
Under the usual conditions (1.2 equiv of C_2Cl_6, NaH), the 12-membered sulfone ester **15** affords a complex mixture of products. This mixture has not been characterized in detail, but the crude NMR spectrum retains only a fraction of the expected carboethoxy signals. When the experiment is performed using excess C_2Cl_6 and potassium *tert*-butoxide as base, the major isolable product (35%) also lacks the carboethoxy group. According to NMR and mass spectral evidence,



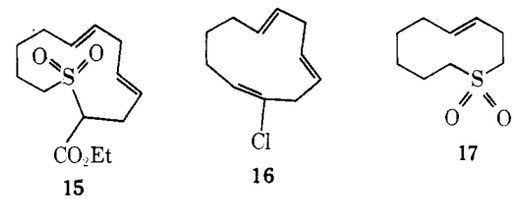
10 **11**



12 **13**



14



15 **16** **17**

0022-3263/78/1943-4884$01.00/0

structure **16** can be assigned to this substance. Apparently, nucleophile-induced decarboxylation is faster than episulfone formation in the 12-membered ring series. Further chlorination and eventual Ramberg–Backlund reaction must then take place to account for the appearance of **16**.

The one-pot Ramberg–Backlund process does not work with simple, unactivated sulfones. Di-*n*-butyl sulfone and the ten-membered ring sulfone **17**[3] are recovered unchanged from treatment with sodium hydride and hexachloroethane.[6]

Experimental Section

Sulfones were prepared from the known sulfides by typical *m*-chloroperbenzoic acid oxidation: sulfone **1**, bp 113–125 °C (0.1 mm, Kugelrohr); **3**, bp 125–130 °C (0.1 mm, Kugelrohr); **10**, mp 54–55 °C (from ether–hexane); **12**, bp 140–150 °C (0.1 mm, Kugelrohr). *E,E* sulfone ester **15** crystallized as the major component from MCPBA oxidation of an *E,E* and *E,Z* mixture of sulfides:[1b] mp 79–80 °C (from ether–hexane); 270 MHz NMR ($CDCl_3$; *J* values based on decoupling experiments) δ 5.7 (1 H, dt, J = 15.6, 7 Hz), 5.45 (1 H, m, J_{vinyl} = 15.1 Hz), 5.34 (1 H, m, J_{vinyl} = 15.6 Hz), 5.22 (1 H, dt, J = 15.6, 7 Hz), 4.15 (2 H, q, J = 7 Hz), 3.82 (1 H, dd, J = 7.3, 3.9 Hz), 3.25 (2 H, m), 2.65–2.8 (4 H, m), 2.16 (2 H, m), 1.85 (2 H, m), 1.57 (2 H, br s), 1.32 (3 H, t, J = 7 Hz); *m/e* 286.12310 (calcd for $C_{14}H_{22}O_4S$, 286.12388). Chloro sulfone ester **4** was obtained from **3** using the standard Ramberg–Backlund procedure (see below): mp 68–70 °C (from hexane); NMR ($CDCl_3$) δ 5.1 (singlet, $HC(Cl)CO_2C_2H_5$); *m/e* 242.03785 (calcd for $C_8H_{15}ClO_4S$, 242.03795).

General Procedure for One-Pot Ramberg–Backlund Sulfur Extrusion. The sulfone (1 mmol) was added to a magnetically stirred suspension of NaH (57% dispersion in oil, washed with hexane; 3.5 mmol) in 10 mL of dimethoxyethane (distilled from $LiAlH_4$) under nitrogen flow. The mixture was cooled in an ice bath and recrystallized. Hexachloroethane (1.2 mmol) was added. After the initial mild exothermic reaction had subsided, the ice bath was removed and the mixture was stirred at 20 °C for 3–24 h. The yellow mixture was then cooled, and water was cautiously added. Extraction with ether (2 × 20 mL), drying ($MgSO_4$), and concentration (aspirator) gave an oily residue. The sulfur extrusion product was then isolated by distillation (Kugelrohr). Unreacted α-chloro sulfone ester remained in the pot residue and was isolated by chromatography (PLC, silica gel). Characterization of carbocyclic sulfur extrusion products follows.

***(E,E)*-2-Carboethoxycycloocta-1,4-diene 11:** foul-smelling liquid; bp 80–90 °C (0.2 mm, Kugelrohr); 100 MHz NMR ($CDCl_3$) δ 6.72 (1 H, br t, J = 8 Hz), 5.8 (1 H, ddd, J = 16, 9, 6 Hz), 5.36 (1 H, ddd, J = 16, 10, 5 Hz), 4.1 (2 H, q, J = 7 Hz), 3.0 (2 H, ABX, J_{AB} = 16 Hz, J_{AX} = 9 Hz, J_{BX} = 5 Hz), 1.3–2.5 (6 H, m), 1.28 (3 H, t); IR (neat) 1705, 985 cm^{-1}; *m/e* 180.11566 (calcd, 180.11503).

***(E,E)*-2-Carboethoxycyclonona-1,4-diene 14:** liquid; bp 115–125 °C (0.2 mm, Kugelrohr); 100 MHz NMR ($CDCl_3$) δ 6.96 (1 H, br t, J = 8 Hz), 5.3–5.8 (2 H, m), 4.2 (2 H, q, J = 7 Hz), 3.5 (1 H, br d, J = 16 Hz), 3.0 (1 H, dd, J = 16, 8 Hz), 1.5–2.6 (7 H, m), 1.3 (3 H, t, J = 7 Hz), 1.1 (1 H, m); IR (neat) 1710, 988 cm^{-1}; *m/e* 194.13050 (calcd for $C_{12}H_{18}O_2$, 194.13068). At 270 MHz, the olefinic region of δ 5.3–5.8 is resolved and a trans vinyl coupling of 15.4 Hz is present.

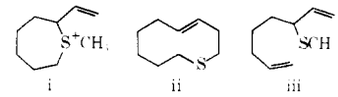
2-Chlorocycloundeca-1,4,7-triene (16). Sulfone ester **15** (30 mg, 0.11 mmol) was dissolved in dry DME (1 mL) and stirred under nitrogen. Potassium *tert*-butoxide (26 mg, 0.23 mmol) and C_2Cl_6 (55 mg, 0.23 mmol) were added. After 16 h at 20 °C, the product was recovered by the usual ether–aqueous workup. Separation by PLC (silica gel, 3% ethyl acetate–hexane) gave a major zone at R_f 0.6 of 7 mg (35%) of **16**. The oily product slowly solidified: mp 66–70 °C; 270 MHz NMR ($CDCl_3$) δ 4.95–5.25 (5 H, m), 2.97 (2 H, m), 2.6–2.75 (2 H, m), 2.33 (1 H, m), 2.11 (3 H, m), 1.6–1.9 (2 H, m); IR (neat) 980, 960 cm^{-1}; *m/e* 182.08607 (calcd for $C_{11}H_{15}Cl$, 182.08623).

Acknowledgment. This work was supported by PHS Grant CA17918-02.

Registry No.—**1**, 66102-12-3; (*E*)-**2**, 22210-20-4; (*Z*)-**2**, 66102-13-4; **3**, 66102-14-5; **4**, 66102-15-6; (*E*)-**7**, 66102-16-7; (*Z*)-**7**, 66102-17-8; **10**, 66102-18-9; **11**, 66102-19-0; **12**, 66102-20-3; **13**, 66102-21-4; **14**, 66102-22-5; **15**, 66102-23-6; **16**, 66102-24-7; hexachloroethane, 67-72-1.

References and Notes

(1) (a) E. Vedejs, J. P. Hagen, B. L. Roach, and K. L. Spear, *J. Org. Chem.*, in press; (b) E. Vedejs, M. J. Arco, D. W. Powell, J. M. Renga, and S. P. Singer, *ibid.*, companion paper, this issue.
(2) J. Kattenberg, E. R. de Waard, and H. O. Huisman, *Tetrahedron Lett.*, 1173 (1977); *Tetrahedron*, **30**, 463 (1974).
(3) The precursor sulfide, (*E*)-thiacyclodec-4-ene, was prepared by a ring expansion sequence starting from 2-vinylthiepane.[1b] Methylation (CH_3OSO_2F) and treatment of the sulfonium salt i with KH at 0 °C give ring expansion product ii and the fragmentation product iii,[4] 7:1 ratio (40%). If $KOC(CH_3)_3$ is used as the base at 20 °C, products are recovered in 81% yield, but the ratio of ii/iii is 1.4:1.



i ii iii

(4) Identical with authentic iii, prepared by methylation of the corresponding mercaptan.[5]
(5) S. P. Singer and J. P. Hagen, unpublished results.
(6) For a one-pot Ramberg–Backlund procedure which succeeds with unactivated sulfones, see C. Y. Meyers, A. M. Malte, and W. S. Matthews, *J. Am. Chem. Soc.*, **91**, 7510 (1969).

Stereoselective Synthesis of (*E*)- and (*Z*)-1-(Phenylseleno)-1-alkenes[1]

Stanley Raucher,* Michael R. Hansen, and Mark A. Colter

Department of Chemistry, University of Washington, Seattle, Washington 98195

Received July 5, 1978

Recently we described a procedure for the preparation of 1-(phenylseleno)-1-alkenes[2] via the addition of phenylselenenyl bromide to monosubstituted alkenes **1** under thermodynamically controlled conditions, followed by dehydrobromination of the resulting Markownikoff adducts **2**. Although this transformation was regioselective, it was not stereoselective; initial experiments involving the dehydrobromination of **2** with potassium *tert*-butoxide in THF led to the formation of both (*E*)-1-(phenylseleno)-1-alkenes **3** and (*Z*)-1-(phenylseleno)-1-alkenes **4** (Table I).

We now wish to report procedures for the stereoselective preparation of both (*E*)- and (*Z*)-1-(phenylseleno)-1-alkenes.

A number of base–solvent systems were examined for the dehydrobromination of **2** in an effort to improve the ratio of *E–Z* isomers. The highest *E–Z* ratios were obtained utilizing lithium diisopropylamide (LDA) in Et_2O at 0 °C (Table I). The presence of even small amounts of THF (10% by vol) in the LDA–Et_2O procedure resulted in *E–Z* ratios similar to

Table I. Percentage of 3/4 Formed by Dehydrobromination of β-Bromoalkyl Phenyl Selenides 2[a]

			reaction conditions[b]		
	β-bromoalkyl phenyl selenide **2**		*t*-BuOK–THF	LDA–Et_2O	registry no. of **3**/registry no. of **4**
entry	R	registry no.	**3**/**4**	**3**/**4**	
a	Me	68001-59-2	55/45	77/23	68001-61-6/ 68001-62-7
b	*n*-Bu	63831-75-4	60/40	91/9	67649-77-8/ 67649-78-9
c	*i*-Pr	66221-89-4	73/27	96/4	67649-79-0/ 68001-63-8
d	*t*-Bu	66221-91-8	100/0		63831-89-0
e	Ph	68001-60-5	100/0		60466-40-2

[a] Percentages determined by VPC analysis on a 24 ft × ⅛ in. 1.5% DEGS on 100/120 Chromosorb G column. Preparations of mixtures of the following *E* and *Z* isomers have been reported: **3a/4a** (ref 8a,2); **3b/4b** (ref 3,2); **3c/4c** (ref 2); **3e/4e** (ref 3). For preparation of **3d**, see ref 2. The preparation of stereoisomerically pure **3e** and **4e** has been reported (ref 3), although the assignment of stereochemistry is clearly incorrect.[10] [b] In all instances, isolated yields of the (phenylseleno)alkenes were >90%.

0022-3263/78/1943-4885$01.00/0