Notes

Olefin Synthesis. Rate Enhancement of the Elimination of Alkyl Aryl Selenoxides by Electron-Withdrawing Substituents

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The synthetic utility of the gentle olefin-forming syn elimination of alkyl phenyl selenoxides has recently been demonstrated by us[1] and others.[2] However, attempts at forming terminal olefins via the decomposition of primary alkyl phenyl selenoxides have been less successful.[3] We now report a modification that provides for facile elimination of primary alkyl aryl selenoxides to olefins.

In a study[4] on the pyrolysis of a series of para-substituted aryl alkyl sulfoxides, Emerson observed that electron-withdrawing substituents increased the rate of olefin formation, whereas electron-donating substituents decreased the rate. These rates were correlated by a Hammett plot giving $\rho = +0.51$. In light of this, we prepared several substituted aryl lauryl selenoxides. Each selenoxide decomposed to olefin at room temperature, and the effect of different substituents on the rate of elimination is shown in Table I. We observed the same pattern as Emerson, in that electron-withdrawing substituents facilitated the selenoxide elimination.[5]

Table I reveals that electron-withdrawing substituents on the aromatic ring increased both the rate of elimination and the final yield of olefin. Since the aryl-substituted selenium reagents are generally more difficult to prepare on a large scale than diphenyl diselenide, use of the former reagents is probably not necessary for simple cases such as lauryl phenyl selenide.[6] However, we and others[3] have found that when there are substituents on the β and/or γ carbons in the alkyl chain, the yield of olefin can be low with the unsubstituted aryl reagent even after several days. In such cases, use of the aryl substituted reagent is essential for a high yield. For example, Table II shows that the *o*-nitro substituted reagent afforded twice the yield of methylenecyclohexane as the unsubstituted reagent.

Table I
Selenoxide Decomposition[a]

Selenide[b]	Temp, °C	Time,[c] hr	Yield, %
2-$NO_2C_6H_4$-SeR (1)	0	0.5	91
2-CF_3-4-$NO_2C_6H_3$SeR (2)	25	0.5	88
4-NO_2-C_6H_4-SeR (3)	25	1.5	93
3-CF_3-C_6H_4-SeR (4)	25	2	70
4-Cl-C_6H_4-SeR (5)	25	6	77
C_6H_5-SeR (6)	25	20	77[d]
4-CH_3O-C_6H_4-SeR (7)	25	7	60

[a] The selenide was dissolved in THF and excess (10 equiv) 30% H_2O_2 was added. Yields of 1-dodecene were determined by GLC relative to an internal standard. [b] The selenides [R = $(CH_2)_{11}CH_3$] were prepared by treating 1-bromododecane with the corresponding ArSeNa species, prepared in situ by reduction of the diselenide[6] (2, 4, 5, 6, 7) or selenocyanate[7] (1, 3) with sodium borohydride in ethanol. [c] These are the approximate times after which further production of olefin was negligible, measured from completion of oxidation as determined by TLC. [d] It should be noted that there is a difference between this yield (77%) and that (6%) previously reported[1a] for this same substrate. We have not been able to reproduce the earlier low yield and at present have no explanation for this discrepancy.

Table II
Selenoxide Decomposition[a]

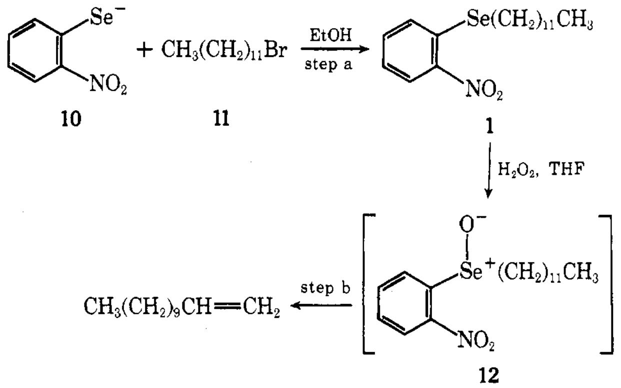
Selenide[b]	Temp, °C	Time, hr	Yield, %	Registry no.
C_6H_5-Se-CH_2-cyclohexyl	25	9.5 48	47 46	53973-68-5
4-Cl-C_6H_4Se-CH_2-cyclohexyl	25	9.5	85	53973-69-6
2-NO_2-C_6H_4-Se-CH_2-cyclohexyl	25	9.5	92	53973-70-9

[a] Reactions were run as given in Table I, footnote *a*. Time was measured from the addition of H_2O_2. Yields of methylenecyclohexane were determined by GLC. [b] The selenides were prepared by treating the tosylate of cyclohexanemethanol with the corresponding selenide anion.

The selection of the best substituted reagent is a compromise between ease of preparation, yield in the alkylation step, and yield in the elimination step. In view of this, *o*-nitrophenyl selenocyanate (13)[8] and 4,4′-dichlorodiphenyl diselenide (14)[9] are among the better reagents. The dichloro diselenide 14 is particularly attractive since it is as easy to prepare as diphenyl diselenide. Although there will undoubtedly be cases where the potent effect of the *o*-nitro substituent will be needed to facilitate elimination, in most instances the of the *p*-chloro substituent should suffice.

A typical procedure is illustrated in Scheme I for the *o*-nitro case. The selenide anion 10 was treated with bromide 11 to afford selenide 1. The selenide was not isolated, but was oxidized by excess hydrogen peroxide to the unstable selenoxide 12, which decomposed readily to 1-dodecene. Results of this one-pot sequence are presented in Table III. Although *o*-nitrophenyl lauryl selenoxide (12) decomposes in higher yield (91%, Table I), the overall yield of olefin is not much higher than that obtained from the other systems. This is due to the lower yield in the alkylation step (step a, Scheme I).

Scheme I



The effect of electron-withdrawing substituents on those synthetic transformations that employ electrophilic seleni-

Table III
Conversion of 1-Bromododecane to 1-Dodecene[a]

Anion precursor	Step a	Step b	Yield, %
2-NO_2-C_6H_4SeCN (**13**)	8 hr	10 hr, 25°	76 (62)
(4-Cl-C_6H_5Se)$_2$ (**14**)	8 hr	10 hr, 25°	70 (62)
(C_6H_5Se)$_2$ (**15**)	8 hr	10 hr, 25°	59

[a] Reactions were run on a 5-mmol scale, analogous to the procedure given in the Experimental Section. Yields of 1-dodecene were determined by GLC, except for those in parentheses, which were determined by isolation.

um reagents[1c,d,2a–c,f,g] is currently being investigated in our laboratory.

Experimental Section

Preparation of 1-Dodecene. To a cooled (ice bath) suspension of *o*-nitrophenyl selenocyanate (**13**, 10.26 g, 0.045 mol) in absolute ethanol (200 ml) in a 500-ml, three-necked, round-bottom flask under nitrogen, sodium borohydride (1.9 g, 0.05 mol) was added in small batches while stirring magnetically. A dark red solution resulted. (Caution! Reduction of the selenocyanate is exothermic and vigorous hydrogen evolution occurs.) 1-Bromododecane (11.15 g, 0.045 mmol) was added and the solution was stirred at room temperature for 8 hr. Tetrahydrofuran (100 ml) was added; and after cooling again in an ice bath, 30% hydrogen peroxide (39 ml, 0.45 mol) was added dropwise over a period of 1 hr. The ice bath was removed and the solution stirred for an additional 8 hr. The mixture was diluted with water and extracted with hexane. The hexane layer was washed with aqueous sodium carbonate and brine, dried ($MgSO_4$), filtered, and concentrated under reduced pressure to give a dark orange oil. Filtration through alumina (hexane) gave upon removal of the solvent a colorless oil, which upon vacuum distillation (83–85°, 7 mm) gave 1-dodecene (4.65 g, 62%).

Preparation of *o*-Nitrophenyl Selenocyanate (13). According to the procedure of Bauer,[8] *o*-nitroaniline (20.7 g, 0.15 mol) was added to 6 *M* HCl (90 ml) contained in a 1-l., three-necked, round-bottom flask fitted with a mechanical stirrer and addition funnel. After stirring for 5 min, the suspension was cooled to 0° and a solution of sodium nitrite (12.4 g, 0.18 mol) in water (60 ml) was slowly added. Urea (3.5 g) was added after 20 min and the reaction was checked with starch–iodide paper. Sodium acetate (25 g) was added to give pH ~ 6 on pH paper. A solution of potassium selenocyanate[10] in water (100 ml) was added slowly, giving a mushy, dark brown solid. The solid was collected, washed with water, recrystallized from 95% ethanol (700 ml), and dried in vacuo to give light brown crystals (22.4 g, 66%), mp 139–141° (lit. mp 142°).

Preparation of Diphenyl Diselenide 15. (All operations should be carried out in a well-ventilated hood.)

In a 3-l., three-necked, round-bottom flask, equipped with a reflux condenser, mechanical stirrer, 2-l. addition funnel, and nitrogen inlet, were placed 58 g (2.43 mol) of magnesium turnings and a crystal of iodine. The apparatus was flamed out under a stream of dry nitrogen and allowed to cool to room temperature.

A solution of bromobenzene (380 g, 2.43 mol) in 1280 ml of anhydrous ether (two 1-lb cans) was placed in the addition funnel. The magnesium was covered with a layer of anhydrous ether and several milliliters of neat bromobenzene were added to initiate the reaction. Once initiated, the reaction was stirred vigorously and the halide added at such a rate as to maintain a gentle reflux (2–2.5 hr). Stirring of the brown solution was continued for 0.5 hr, and the dropping funnel was replaced with a glass stopper.

Powdered black selenium [192 g, 2.43 mol (B & A)] was added in 1–2-g portions (exothermic) to the vigorously stirred solution, over a 2.5-hr period; the resulting gray-green suspension was stirred for 0.5 hr.

The mixture was poured into a 6-l. erlenmeyer flask containing 4 l. of crushed ice; concentrated hydrochloric acid (375 ml) was then slowly added with swirling until all of the ice had melted. The contents of the flask were poured into a 6-l. separatory funnel, the aqueous layer was removed and extracted once with 400 ml of ether, and the combined organic layers were filtered through a Celite pad into a 4-l. filtration flask. To the dark orange solution, in the same flask, 1600 ml of 95% ethanol, five pellets of potassium hydroxide, and a 3-in. magnetic stirring bar were added. The flask was stoppered with a one-hole cork, and a glass tube inserted, until it just reached the surface of the liquid. Air was drawn rapidly over the vigorously stirred solution until a thick yellow precipitate was formed and the odor of selenophenol had disappeared. For convenience, the oxidation was allowed to proceed overnight, permitting most of the ether to evaporate.

The yellow slurry was filtered on a 160-mm Büchner funnel, washed several times with cold 95% ethanol, sucked as dry as possible, then dried overnight under a high vacuum at 40° to afford 286 g (75%) of the bright yellow diselenide (mp 63–65°).

The ethanol filtrate may be concentrated on a rotary evaporator to yield a second crop of diselenide; the total yield is then raised to 77–80%. The residual red oil may be vacuum distilled to afford diphenyl selenide (167°, 16 mm), a by-product of this preparation.

Diphenyl diselenide prepared in this manner is a bright yellow, crystalline, air-stable compound, with a faint odor. It is sufficiently pure for all subsequent reactions; purer material may be obtained by recrystallization from hexanes.

The above procedure is a modification of a procedure[11] for the preparation of selenophenol.

Preparation of 4,4′-Dichlorodiphenyl Diselenide (14). This light-orange solid was prepared in 75% yield from *p*-bromochlorobenzene following exactly the same procedure as given above for the preparation of diphenyl diselenide.

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Registry No.—**1,** 53973-63-0; **2,** 53973-64-1; **3,** 53973-65-2; **4,** 54019-82-8; **5,** 53973-66-3; **6,** 42066-69-3; **7,** 53973-67-4; **10,** 54019-83-9; **11,** 112-29-8; **13,** 51694-22-5; **14,** 20541-49-5; **15,** 1666-13-3; 1-dodecene, 112-41-4; sodium borohydride, 16940-66-2; bromobenzene, 108-86-1; selenium, 7782-49-2; *p*-bromochlorobenzene, 106-39-8; sodium *o*-nitrobenzenoselenol, 53973-71-0; sodium 2-(trifluoromethyl)-4-nitrobenzeneselenol, 53973-72-1; sodium *p*-nitrobenzeneselenol, 53973-73-2; sodium *m*-(trifluoromethyl)benzeneselenol, 37773-11-8; sodium *p*-chlorobenzeneselenol, 41491-33-2; sodium benzeneselenol, 23974-72-3; sodium *p*-methoxybenzeneselenol, 41422-62-2; bis[4-nitro-2-(trifluoromethyl)phenyl] diselenide, 53973-74-3; bis[*m*-(trifluoromethyl)phenyl] diselenide, 53973-75-4; bis(*p*-methoxyphenyl) diselenide, 38762-70-8; *p*-nitrophenylselenocyanate, 19188-18-2; methylenecyclohexane, 1192-37-6; tosylate of cyclohexanemethanol, 3725-11-9; phenylselenide anion, 14971-39-2; *p*-chlorophenylselenide anion, 54019-84-0; KSeCN, 3425-46-5; 2-chloro-5-nitrobenzotrifluoride, 777-37-7.

References and Notes

(1) (a) K. B. Sharpless, M. W. Young, and R. F. Lauer, *Tetrahedron Lett.*, 1979 (1973); (b) K. B. Sharpless and R. F. Lauer, *J. Am. Chem. Soc.*, **95,** 2697 (1973); (c) K. B. Sharpless, R. F. Lauer, and A. Y. Teranishi, *ibid.*, **95,** 6137 (1973); (d) K. B. Sharpless and R. F. Lauer, *J. Org. Chem.*, **39,** 429 (1974).

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(3) Private communications from Professor Dieter Seebach (Justus Liebig Universität), Professor Paul Grieco (University of Pittsburgh), and Professor Paul Dowd (University of Pittsburgh).

(4) D. W. Emerson and T. J. Korniski, *J. Org. Chem.*, **34,** 4115 (1969).

(5) We were recently informed that three other research groups have independently discovered that electron-withdrawing substituents accelerate these selenoxide eliminations: private communications from Professor H. J. Reich (University of Wisconsin), Professor D. Seebach (Justus Liebig Universität), and Professor R. H. Schlessinger (University of Rochester).

(6) 4,4′-Dimethoxydiphenyl diselenide (ref 7, p 1095) and bis(2-trifluoromethylphenyl) diselenide were prepared on a 25-mmol scale (based on the corresponding aryl bromide) analogous to the procedure for diphenyl diselenide. Bis(2-trifluoromethyl-4-nitrophenyl) diselenide was prepared by refluxing a solution of KSeCN (prepared in situ by heating potassium cyanide and gray selenium powder in DMAC) and 2-chloro-5-nitrobenzotrifluoride in DMAC for 4 hr. The mixture was poured into water and the solid collected by filtration. The dark brown solid was extracted into hot CH_2Cl_2 and filtered. After the solvent was removed, the resulting green

solid was recrystallized from absolute ethanol to give yellow-green needles (67%), mp 136–137°.
(7) Houben-Weyl, "Methoden der Organischen Chemie", Band IX, Georg Thieme Verlag, Stuttgart, 1955, p 944.
(8) H. Bauer, *Ber.*, **46**, 92 (1913).
(9) Reference 7, p 1096.
(10) The potassium selenocyanate used in this preparation was made according to G. R. Waitkins and R. Shutt, *Inorg. Synth.*, **2**, 186 (1946).
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Acid-Catalyzed Hydrolysis of Amidosulfites

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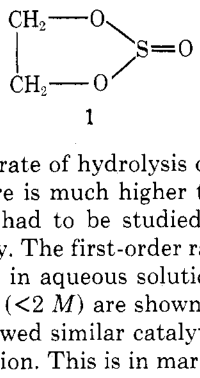
The mechanisms of the acid-catalyzed hydrolysis of cyclic sulfites, e.g., ethylene sulfite (1), have been studied in some detail.[1] Only recently have successful syntheses been described of the analogous cyclic amidosulfites.[2,3] They hydrolyze in strong acid to the corresponding amino alcohol.[3] We now report the first kinetic study of the acid-catalyzed ring opening of this class of compound on 3-*tert*-butyl-1,2,3-oxathiazolidine 2-oxide (2).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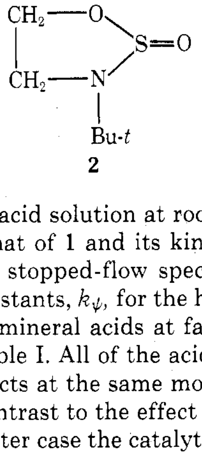
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The rate of hydrolysis of 2 in acid solution at room temperature is much higher than that of 1 and its kinetic behavior had to be studied using stopped-flow spectrophotometry. The first-order rate constants, k_ψ, for the hydrolysis of 2 in aqueous solutions of mineral acids at fairly low acidity (<2 *M*) are shown in Table I. All of the acids studied showed similar catalytic effects at the same molar concentration. This is in marked contrast to the effect of acids on the hydrolyses of 1. In this latter case the catalytic effect of the acids falls in the order HBr > HCl > $HClO_4$ because ethylene sulfite hydrolyzes by both a bimolecular (A2) and a nucleophilic catalysis mechanism.

Table I
Hydrolysis Rate, k_ψ (sec^{-1}), of 2 in Aqueous Mineral Acids

$HClO_4$ Concn, *M*, at 22°						
0.10	0.20	0.52	0.72	1.04	1.56	2.06
0.59	1.09	2.85	4.36	6.84	11.0	15.4
HCl Concn, *M*, at 22°						
0.10	0.20	0.50	0.70	1.00	1.50	2.00
0.49	1.17	2.92	4.18	6.29	10.7	15.1
HBr Concn, *M*, at 22°						
0.16	0.40	0.56	0.80	0.96	1.20	1.60
0.91	2.37	3.36	5.21	6.40	8.21	12.0
$HClO_4$ (0.52 *M*) at Various Temp, °C						
14.2	21.0	25.0	28.9	33.9	39.7	
1.99	2.85	3.96	4.93	6.39	9.85	

Analysis of the kinetic data for the hydrolysis of 2 shown in Table I in terms of the Bunnett approach[4] leads to a *w* value of 6.8, suggesting that water is acting both as a nucleophile and a proton transfer agent. The entropy of activation, $\Delta S^\ddagger$ (−19.1 ± 1.4 eu), calculated from the data in Table I also falls in the range associated with a bimolecular rate-determining step.[5]

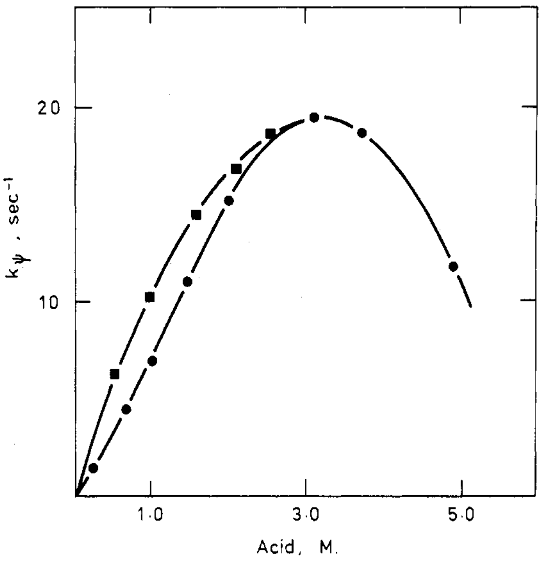
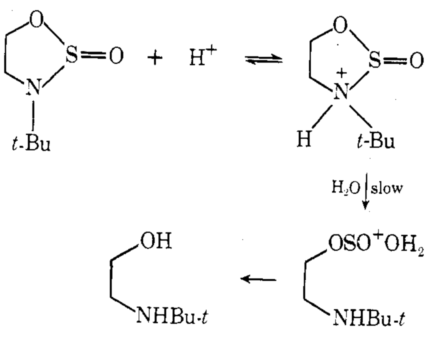


Figure 1. Hydrolysis of 2 in water at 22°: ●, $HClO_4$; ■, $HClO_4$ + $NaClO_4$ (3.0 *M*).

At higher concentrations of perchloric acid (>2 *M*) the rate of hydrolysis of 2 goes through a maximum, as shown in Figure 1. Such rate maxima can arise in two common ways, either as a result of extensive protonation of a basic substrate as in the hydrolysis of amides[6] or the superposition of a specific salt effect on an acid-catalyzed reaction such as observed in the hydrolysis of some sulfites,[7] phosphates,[8] and phosphinates.[9] In mixtures of perchloric acid and sodium perchlorate at constant ionic strength (Figure 1) the rate at first increases linearly with increase in acid concentration and then curves over. Similar behavior has been observed in the hydrolysis of amides and related compounds, e.g., hydroxamic acids, and has been attributed to extensive protonation of the substrate.[10] Such a view is supported by the values of the kinetic solvent isotope effect, $k_1^{D_2O}/k_1^{H_2O}$ (KSIE), which are 1.16, 0.67, and 0.58 at 0.516, 4.26, and 4.61 *M* perchloric acid, respectively (compargd at the same molar concentration of acid). A similar fall of the KSIE with increasing acidity observed for the hydrolysis of amides has been discussed by Bell[11] and Wiberg[12] in terms of the increasing extent of protonation of the substrate and the weaker nucleophilic reactivity of D_2O compared to H_2O.

The kinetic behavior of 2, in particular the absence of nucleophilic catalysis, the occurrence of a rate maximum, and the high reactivity of 2 in acid solution, contrasts markedly with that of ethylene sulfite and suggests a different mechanism. One possible mechanism consistent with such behavior assumes a rapid preequilibrium protonation of 2 in which protonation is assumed to occur on nitrogen followed by slow rate-determining attack of a water molecule at sulfur (eq 1 and 2). The high reactivity of 2 and the


(1)
(2)