obtained as a light yellow oil: IR (neat) 1610 cm^{-1}; NMR ($CDCl_3$) δ 0.90–2.08 (m, 10, cyclohexyl CH_2), 2.58 (t, 2, CH_2), 2.80 (m, 1, cyclohexyl CH), 3.60 (t, 2, benzylic CH_2), 6.95–7.65 (m, 4, ArH). Anal. Calcd for $C_{15}H_{19}N$: C, 84.51; H, 8.92; N, 6.57. Found: C, 84.58; H, 9.03; N, 6.36.

Reaction of (2) with Phenylacetonitrile. The general procedure was followed except that an excess (0.6 mol) of phenylacetonitrile was added to 0.2 mol of **2.** The basic fraction was negligible but the neutral fraction on vacuum distillation yielded phenylacetonitrile (88% recovery) and 1,3-diphenylbutyronitrile (**5**) (1.55 g, 35% yield based on **1**, bp 126–128 °C (0.10 Torr)): IR (neat) 2230 cm^{-1}; NMR ($CDCl_3$) δ 2.12 (m, 2, CH_2CH), 2.80 (t, 2, benzylic CH_2), 3.64 (t, 1, CH), 7.00–7.68 (m, 10, ArH). Anal. Calcd for $C_{16}H_{15}N$: C, 86.88; H, 6.79; N, 6.33. Found: C, 86.63; H, 7.00; N, 6.35.

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Registry No.—**1**, 1074-15-3; **2**, 57918-65-7; **4a**, 52250-50-7; **4b**, 59224-73-; **4b** picrate, 65071-49-0; **4c**, 65071-50-3; **4c** picrate, 65071-51-4; **4d**, 65071-52-5; **5**, 5558-42-9.

References and Notes

(1) This paper is dedicated to the memory of Dr. W. E. Parham, deceased May 21, 1976.
(2) Supported by the U.S. Army Research Office through Grant DAHC04 74 GD128.
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(9) The low temperature was employed to make halogen–metal exchange more selective and to hold at a minimum the formation of benzocyclobutene (ref 3c).
(10) GLC analyses were carried out on a column of 20% SE-30 on 60/80 Chromosorb W [4 ft × 0.25 in., 250 °C, 30 mL/min He]. Preparative GLC appeared preferable to distillation in dealing with small volumes of product. Positive identification of the products was effected by NMR as well as by elemental analysis on either the picrate or the free base.
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Selenium in Synthesis. Conjugated Vinylic Ethers, Esters, and Halides from α-Hetero-Substituted Selenides

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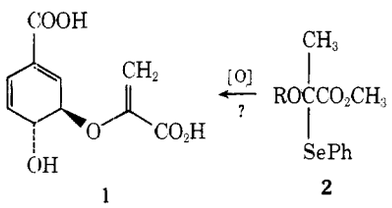
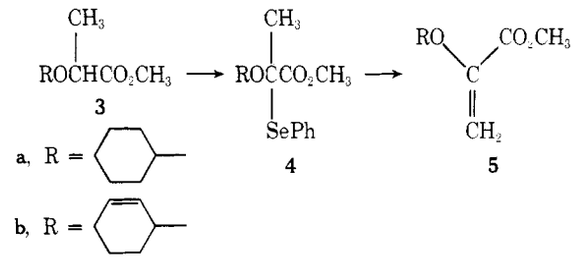
Recent work in our laboratory aimed at the total synthesis of chorismic acid **1**[1] has led us to investigate the oxidative fragmentation of α-oxygenated α-phenylseleno carboxyl derivatives **2** as an approach to the sensitive enol pyruvyl functionality in **1**.[2] Although there have been numerous reports of arylseleno carbonyl compounds serving as precursors for α,β-unsaturated ketones and esters,[3] the effect of an additional heteroatom on such selenoxide eliminations appears not to have been studied. In this note we disclose that α-alkoxy as well as α-acyloxy and α-chloro-unsaturated esters can be prepared from appropriately substituted selenides at neutral pH and below room temperature.



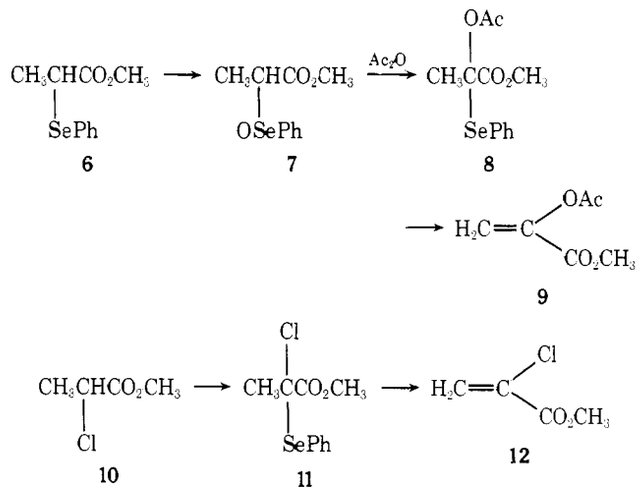
1 2

Cyclohexanol and 2-cyclohexen-1-ol were converted to α-alkoxypropionates **3a** and **3b** by the classical Williamson ether synthesis. Selenation of the corresponding ester enolates



(LDA, THF–HMPA, −70 °C) using phenylselenenyl bromide or diphenyl diselenide afforded **4a** and **4b** without complication. When solutions of these arylseleno esters in ethyl acetate were treated with 30% H_2O_2 (4–6 equiv) at 0 °C for 2 h, the enol pyruvates **5a** and **5b** were produced in 30 and 36% yields, respectively, after column chromatography.

In related experiments we had occasion to prepare two other hetero-substituted selenides. Acyloxyseleno ester **8** arose from the low-temperature Pummerer reaction of selenoxide **7**.[4]



Chloroseleno ester **11** was synthesized by metalation and selenation of methyl α-chloropropionate. Both **8** and **11** underwent smooth oxidation and rapid elimination at 0 °C to produce the known α-acetoxy and α-chloroacrylic esters **9**[5] and **12**.[6]

Unsaturated carbonyl compounds bearing α-oxygen or α-halogen substituents are relatively unstable substances. The very gentle reaction conditions we have delineated constitute a convenient access to these structures.[7,8]

Experimental Section[9]

Selenation of Methyl 2-Cyclohexyloxypropionate. Preparation of 4a and Oxidation to 5a. A solution of LDA (1.2 mmol) was prepared in THF (5 mL) from diisopropylamine (0.168 mL) and *n*-BuLi (0.83 mL of a 1.45 M solution in hexane), then cooled to −70 °C under N_2. To it was added a solution of **3a** (0.186 g, 1.0 mmol) and HMPA (0.358 g, 2 mmol) in THF (1 mL) and the reaction mixture was stirred for 1 h. Meanwhile a solution of PhSeBr was prepared from PhSeSePh (0.47 g, 1.5 mmol) and Br_2 (0.24 g, 1.5 mmol) in THF (3.5 mL). A portion of this solution (1.4 mL, ca. 1.2 mmol of PhSeBr) was added by syringe to the enolate anion at −60 to −70 °C and the dark

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mixture was stirred for 3 h at −70 °C. After warming to room temperature, 10% NH_4Cl was added and the aqueous layer extracted 3 times with ether. The combined organic layers were washed with 5% HCl, 5% $NaHCO_3$, and water, then dried over $MgSO_4$. Filtration and evaporation yielded 0.31 g of yellow oil: NMR δ 1.75 (s, 3 H), 3.56 (s, 3 H), 3.6–3.7 (m, 1 H), 7.30, 7.52 (2m, 5 H); IR λ_{max} 5.77 μm.

The crude selenoester was dissolved in ethyl acetate (6 mL) and with ice-cooling, 30% H_2O_2 (0.6 mL, 5.3 mmol) was added cautiously. After stirring for 2 h at 0 °C, the reaction mixture was diluted with water (10 mL) and extracted twice with ether. The organic extracts were washed with 10% $NaHSO_3$, 5% $NaHCO_3$, and water. Drying ($MgSO_4$), filtration, and concentration afforded 0.11 g of an oil. Column chromatography (10 g silica gel, $CHCl_3$) was used to elute the desired product **5a** (55 mg, 30%) having R_f = 0.6 in $CHCl_3$: NMR δ 5.37 (d, 1 H, J = 2 Hz), 4.58 (d, 1 H, J = 2 Hz), 3.76 (s, 3 H), 3.8–4.05 (m, 1 H); IR λ_{max} 5.80, 6.16 μm. This material was identical in every respect with an authentic sample of **5a** prepared by the anionic condensation of methyl cyclohexyloxyacetate with formaldehyde, then dehydration.

Selenation of Methyl 2-(2-Cyclohexen-1-yl)oxypropionate. Preparation of 4b and Oxidation to 5b. A solution of LDA (1.8 mmol) was prepared as usual from diisopropylamine (0.252 mL) and n-BuLi (1.125 mL of a 1.6 M solution) in THF (6.5 mL), then cooled to −70 °C under N_2. A mixture of **3b** (0.276 g, 1.5 mmol) and HMPA (0.537 g, 3 mmol) in THF (1.5 mL) was added slowly and the colorless solution was stirred for 1 h at −70 °C. Then PhSeSePh (0.562 g, 1.8 mmol) in THF (1.5 mL) was introduced and after 1 h at −70 °C followed by 3 h at −40 °C, the reaction was terminated by adding 10% NH_4Cl (10 mL). Three ether extracts were combined and washed with 5% HCl, 5% $NaHCO_3$, and water. Drying ($MgSO_4$), filtration, and concentration afforded 0.60 g of yellow oil: NMR δ 1.80 (s, 3 H), 3.55 (s, 3 H), 4.4–4.5 (broad m, 1 H), 5.75 (broad s, 2 H), 7.33, 7.55 (2 m, 5 H); IR λ_{max} 5.77 μm.

The crude product was dissolved in ethyl acetate (9 mL) and cooled to 0 °C. Thirty percent H_2O_2 (0.8 ml, 7 mmol) was added slowly, the reaction mixture stirred 2 h at 0 °C, then worked up by diluting with water (10 mL) and extracting twice, with ether. The combined ether layers were washed with cold $NaHCO_3$ and water, then dried over $MgSO_4$. Filtration and evaporation furnished 0.199 g of oil. TLC showed a UV active spot having R_f = 0.5 in $CHCl_3$. The crude product was chromatographed on a column of silica gel (10 g) using $CHCl_3$ to afford 0.099 g of clear, colorless **5b** (36%): NMR δ 5.82 (broad s, 2 H), 5.38 (d, 1 H, J = 2 Hz), 4.63 (d, 2 H, J = 2 Hz), 4.50 (broad m, 1 H), 3.77 (s, 3 H); IR λ_{max} 5.79, 6.17 μm. This substance was identical in every respect with an authentic sample of **5b** prepared by the condensation of methyl cyclohexenyloxyacetate with formaldehyde, then dehydration.

Preparation of Acetoxyselenide 8. Oxidation of 8 to 9. A solution of methyl 2-phenylselenopropionate (0.30 g, 1.24 mmol) in THF (3 mL) was cooled to −22 °C under N_2 and treated with powdered m-chloroperoxybenzoic acid (85%; 0.251 g, 1.24 mmol). After 30 min, acetic anhydride (0.152 g, 1.49 mmol) was added by microsyringe followed by pyridine (0.216 g, 2.73 mmol). The contents of the flask were stirred for 1 h at −20 °C then 2 h at 0 °C. Ether was added and the organic layer separated, washed with 5% $NaHCO_3$ and water, and finally dried ($MgSO_4$). Filtration and concentration afforded 0.40 g of an oil. This crude product was chromatographed on a column of silica gel (15 g) eluting with $CHCl_3$. Two major fractions were collected. First, 0.050 g (11%) of oil having R_f = 0.65 in $CHCl_3$ was eluted whose structure was shown to be methyl 2-(m-chlorobenzoyloxy)-2-phenylselenopropionate. Continued elution afforded 0.120 g (32%) of **8** as a colorless oil: NMR δ 1.83 (s, 3 H), 2.03 (s, 3 H), 3.59 (s, 3 H), 7.32, 7.60 (2m, 5 H); IR λ_{max} 5.78 μm (broad).

The above sample of **8** was dissolved in ethyl acetate (2.5 mL) and oxidized at 0 °C for 2 h with 30% H_2O_2 (0.3 mL). Workup as described above afforded 0.025 g of pure acetoxyacrylic ester **9** (44%): NMR δ 6.05 (d, 1 H, J = 2 Hz), 5.46 (d, 1 H, J = 2 Hz), 3.82 (s, 3 H), 2.23 (s, 3 H); IR λ_{max} 5.65, 5.78, 6.09 μm. These values are essentially identical with those reported[6] for an authentic sample of **9**.

Preparation of Chloroselenide 11. Oxidation of 11 to 12. A THF (30 mL) solution of LDA was prepared as usual from diisopropylamine (1.54 mL) and n-BuLi (6.9 mL of a 1.6 M solution) and cooled to −78 °C under N_2. To it was added a solution of methyl α-chloropropionate (1.225 g, 10 mmol) in THF (10 mL) with stirring over 1 h. Meanwhile PhSeBr was prepared from PhSeSePh (1.72 g, 5.5 mmol) and Br_2 (.88 g, 5.5 mmol) in THF (10 mL) at 0 °C. The selenating agent was then taken up in a syringe and added rapidly dropwise to the −70 °C enolate solution. After an additional hour at −70 °C the reaction mixture warmed slowly to room temperature and was poured into cold 10% NH_4Cl. Three ether extractions were performed and the combined organic layers were washed with 5% HCl, H_2O, 5% $NaHCO_3$, and saturated NaCl solution. Drying ($MgSO_4$), filtration, and concentration afforded 2.9 g of yellow oil. Using silica gel column chromatography, the major product **11** (R_f 0.6 in $CHCl_3$) was isolated (0.69 g, 69%) as a very pale yellow oil: NMR δ 2.05 (s, 3 H), 3.65 (s, 3 H), 7.35, 7.65 (2m, 5 H); IR λ_{max} 5.76 μm.

A portion of this sample (0.15 g, .54 mmol) was dissolved in ethyl acetate (3 mL) and treated with 30% H_2O_2 (0.31 mL) at 0 °C for 2 h. Workup in the standard fashion with precautions to prevent loss of the low-boiling product gave a concentrate of **12** containing some diethyl ether solvent: NMR δ 6.47 (d, 1 H, J = 2 Hz), 5.97 (d, 1 H, J = 2 Hz), 3.74 (s, 3 H), 1.97 (s, 3 H). These spectral data were identical with an authentic sample of **12** prepared according to Nield.[10]

Acknowledgment. We thank the National Institutes of Health and Eli Lilly & Company for partial support of this research.

Registry No.—**3a,** 65275-60-7; **3b,** 65275-61-8; **4a,** 65275-62-9; **4b,** 65275-63-0; **5a,** 65275-64-1; **5b,** 65275-65-2; **6,** 65275-66-3; **7,** 686-46-4; **8,** 65275-67-4; **10,** 17639-93-9; **11,** 65275-68-5; **12,** 80-63-7; PhSeBr, 34837-55-3; PhSeSePh, 1666-13-3; methyl 2-(m-chlorobenzoyloxy)-2-phenylselenopropionate, 65275-69-6.

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Nitration of *N*-Alkylphthalimides

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The nitration of N-methylphthalimide (**1a**) and N-ethylphthalimide (**1b**) has been reported to give "almost exclusively" the 4-nitro derivative, **2.**[1] However, no details of reaction conditions, actual isomer distributions, or the yields of nitrated products were presented. We recently investigated this reaction in an effort to develop a high-yield synthesis of 4-nitro-N-alkylphthalimides,[2] and we wish at this time to report our results.

We initially nitrated **1a,** slightly modifying the conditions described for the nitration of phthalimide,[3] to give an 85–90% yield of pure **2a.** If the reaction time was reduced from 16 to 2 h, similar results were obtained (see Table I), but a small amount of 3-nitro isomer, **3a,** was obtained. Although the re-

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