71.2, 55.4, 36.1, 21.1; mass spectrum, m/e 128 (M^+), 113, 100, 87.

4,6-Dideoxy-3-*O*-methyl-*dl*-*xylo*-hexopyranose (Chalcose, 8). To a solution of 149 mg (1.16 mM) of methyl ether **3** in 10 mL of THF at room temperature were added 264 mg (2.26 mM) of *N*-methylmorpholine oxide and 0.200 mL of OsO_4 (0.39 M in THF). After the mixture was stirred 15 h, the volatiles were evaporated, and the residue was filtered through silica (~3.0 g) with 20% MeOH/ethyl acetate. The first two column volumes were combined and the solvents removed to give 180 mg (95%) of *dl*-chalcose: IR 3300–3500, 1050 cm^{-1}; ^1H NMR ($CDCl_3$, 90 MHz) δ 5.27 (br m, 0.5 H), 4.55 (br m, 0.5 H), 4.05–4.40 (m, 1 H), 3.1–3.7 (m, 5 H including a singlet at 3.44), 1.8–2.2 (m, 2 H), 1.15–1.40 (m, 5 H, including an apparent triplet); ^{13}C NMR δ 97.3, 93.4, 80.5, 73.3, 68.8, 64.6, 57.4, 37.5, 21.5; mass spectrum, m/e 145 ($M^+ - 17$), 127.

α- and β-Methylchalcosides (9 and 10). To a solution of 180 mg of **8** (1.11 mM) in 10 mL of methanol was added 1 drop of concentrated H_2SO_4. The reaction was stirred at room temperature and monitored for disappearance of starting material. After 2 days, an excess of solid potassium carbonate was added, the mixture filtered, and the residue chromatographed[7] with 3% methanol in ethyl acetate to give 137 mg (70%) of a mixture of **9** and **10** and 5% of recovered starting material. The 1:1 mixture of **9** and **10** was separated on a 3.9 mm i.d. × 30 cm μ-Bondapak CN column with 5% ethyl acetate in hexane. For **9**: IR 3300–3500 cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz) δ 4.77 (d, 1 H, J = 3 Hz) 3.87 (m, 1 H), 3.45–3.51 (m, 2 H) 3.43 (s, 3 H), 3.42 (s, 3 H), 2.35 (br d, 1 H), 2.10 (m, 1 H), 1.26 (br m, 1 H), 1.20 (d, 3 H, J = 6.5 Hz); ^{13}C NMR 100.45, 78.2, 73.5, 64.4, 55.6, 37.7, 21.5. For **10**: IR 3300–3500 cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz) δ 4.13 (d, 1 H, J = 7 Hz), 3.25–3.59 (m, 9 H, including singlets at 3.56 and 3.44), 2.63 (br s, 1 H), 2.10 (m, 1 H), 1.28 (d, 3 H, J = 6.5 Hz), 1.20–1.30 (m, 1 H); ^{13}C NMR δ 104.3, 80.5, 75.1, 68.53, 57.4, 37.6, 21.5; mp 69–70 °C.

Registry No. 1 (R = Me), 75-07-0; **2**, 59414-23-2; **3** (R = Me), 80754-64-9; (±)-**5**, 80754-65-0; (±)-**6**, 80754-66-1; (±)-**7**, 80754-67-2; (*dl*)-**8**, 62222-48-4; (DL)-**9**, 28072-66-4; (*dl*)-**10**, 28072-67-5.

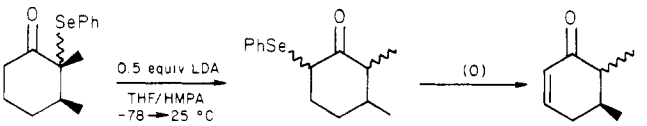
Communications

Based-Induced Rearrangements of α-Phenylselenenyl Ketones

Summary: The formal 1,3 sigmatropic rearrangement of the phenylseleno group of various α-phenylselenenyl ketones proceeds in high yield and thereby permits easy access to α′,β′-unsaturated ketones.

Sir: α-Phenylselenenyl ketones are versatile synthetic intermediates which can be selectively converted into a number of different ketones and enones in high overall yields.[1] In part, the versatility of these species hinges on the ability of an arylseleno group to stabilize an adjacent negative charge,[2] thereby effectively surpressing enolate exchange processes and permitting regiospecific alkylation. Moreover, after alkylation one possesses the option of removing the arylseleno group either oxidatively to produce an enone or reductively to produce to ketone. In this communication we report that under the proper experimental conditions one can effect formal 1,3 sigmatropic rearrangements of the phenylseleno group of an α-phenylselenenyl ketone and, as a consequence, further extend the versatility of these species. An illustration of this process is given below. Specific results are listed in Table I.

When an epimeric mixture of 1^{1a} is treated with 0.5 equiv of lithium diisopropylamide (LDA) in THF containing 2.0 equiv of hexamethylphosphoramide (HMPA) at −78 °C



2 3

and the resulting solution is allowed to slowly warm to room temperature, one isolates after workup an epimeric mixture of **2** in quantitative yield. Confirmation of the structure of **2** is achieved inter alia by its conversion to **3** via the now standard oxidative elimination procedure.[3] Mechanistically we believe the conversion of **1** to **2** occurs via a series of *intermolecular* phenylseleno and proton exchange processes whose driving force is the production of increasingly more stable enolate ions (vide infra).[4] The intermolecular nature of these exchange processes is readily established by varying the concentration of LDA used and qualitatively noting the rate of the reaction.[5] Consistent with a bimolecular process, the fastest "rates" are obtained with 0.5 equiv of LDA.[6] More convincingly, *if a full equivalent of LDA is used, no reaction occurs.*

From a synthetic point of view, these rearrangements proceed in excellent yields with a variety of structurally diverse α-phenylselenenyl ketones (see Table I). In all cases the products consist of mixtures which are epimeric at one or both α-carbon atoms. Since in subsequent synthetic manipulations these mixtures are subjected to

(1) (a) Zima, G.; Barnum, C.; Liotta, D. *J. Org. Chem.* **1980**, *45*, 2737. (b) Reich, H. J.; Renga, J. M.; Reich, I. L. *J. Am. Chem. Soc.* **1975**, *97*, 5434. (c) Grieco, P. A.; Nishizawa, M.; Oguiri, T.; Burke, S.; Marinovic, N. *J. Am. Chem. Soc.* **1977**, *99*, 5773.

(2) Bordwell, F. G.; Bares, J. E.; Bartmess, J. E.; Daucher, G. E.; Gerhold, J.; McCollum, G. J.; Van Der Puy, M.; Vanier, N. R.; Matthews, W. S. *J. Org. Chem.* **1977**, *42*, 326.

(3) (a) Reich, H. J.; Wollowitz, S.; Trend, J. E.; Chow, F.; Wendelborn, D. F. *J. Org. Chem.* **1978**, *43*, 1697.

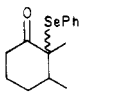
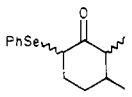
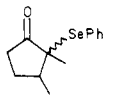
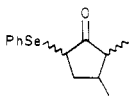
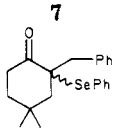
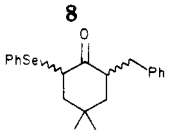
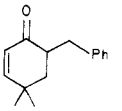
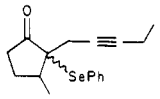
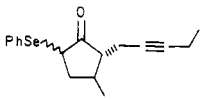
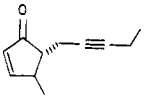
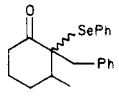
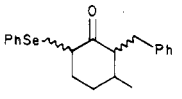
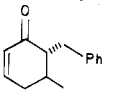
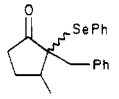
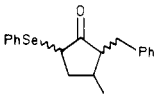
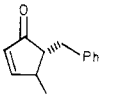
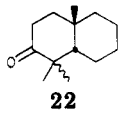
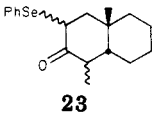
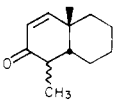
(4) For simplicity, these processes are illustrated as if they occur intramolecularly. A similar rearrangement with 2-(carbomethoxy)-2-(phenylseleno)cyclohexanone has been previously reported. See: Falcone, S. J.; Munk, M. E. *Synth. Commun.* **1979**, *9*, 719.

(5) This is done by varying the amounts of LDA used and then determining the amount of product formed under a standard set of conditions.

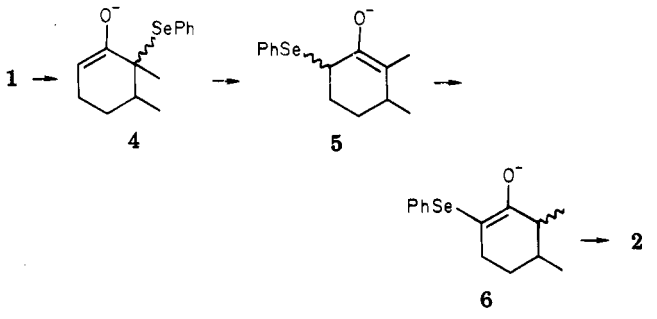
(6) It should be noted that although these processes involve only 0.5 equiv of LDA, at any given time there are also a variety of weaker bases present which also may participate in the overall process. These include **4–6**, as well as diisopropylamine.

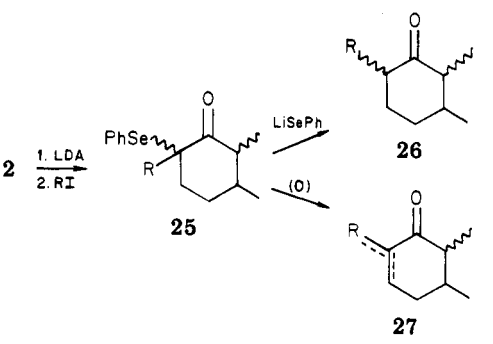
0022-3263/82/1947-1598$01.25/0

Table I

substrate	migration product [a]	% yield [b]	enone [a]	% yield [b]
 1	 2	100	 3	90 [d]
 7	 8	95	 9	85 [d]
 10	 11	92	 12	93 [d]
 13	 14	100	 15	100 [c]
 16	 17	100	 18	90 [d]
 19	 20	92	 21	77 [d]
 22	 23	100	 24	90 [d]

[a] Products were identified by analysis of their IR, NMR, and mass spectra and in some cases by comparison with authentic samples. All new compounds exhibited satisfactory elemental analyses or precise mass determinations. [b] All reported yields are isolated yields. [c] Oxidant = 30% H_2O_2/CH_2Cl_2. [d] Oxidant = $O_3/CH_2Cl_2/-78\,°C$; then, Et_2NH, CH_2Cl_2, Δ.





conditions which can cause equilibration of the epimers, no attempts were made at this stage to either further epimerize the mixtures or to separate the various components of these mixtures. In general, after rearrangement one has available the following options: (a) oxidative elimination of the phenylseleno group to form the corresponding α′,β′-unsaturated ketones (e.g., 2 → 3) or (b) regiospecific α′ alkylation, followed by either oxidative or reductive removal of the phenylseleno group (e.g., 2 → 26 or 2 → 27).[1]

Some comments regarding the examples reported in Table I are noteworthy. First, the conversion of 13 to 15 proceeds quantitatively and represents a key part of our synthesis of *cis*-jasmone,[7] which was accomplished in 76% overall yield from 2-(phenylselenenyl)cyclopentenone (28).[8]

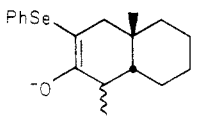
Interestingly, while the conversion of 14 to 15 proceeds smoothly with 30% H_2O_2, all attempts to use this reagent for the conversion of 8 to 9 resulted in the formation of complex mixtures which contained only small amounts of the desired enone.[9] Second, formation of 23 from 22 not only provides easy access to octalone 24 but also enables one to selectively form enolate 29, rather than the enolate 30 which is usually preferred in *cis*-2-decalones.[10] This was demonstrated by converting 23 to 31 in 80% yield. None of regioisomer 32 was isolated.

(7) Liotta, D.; Barnum, C.; Saindane, M. *J. Org. Chem.* **1981**, *46*, 4301.

(8) (a) Zima, G.; Liotta, D. *Synth. Commun.* **1979**, *9*, 697. (b) Shumizer, M.; Takeda, R.; Kuwajima, I. *Tetrahedron Lett.* **1979**, 3461.

(9) See also: Williams, J. R.; Leber, J. D. *Synthesis* **1977**, 427.

(10) Compound 22 was prepared regiospecifically by the direct phenylselenation of the enolate derived from 1,10-dimethyl-*cis*-2-decalone.



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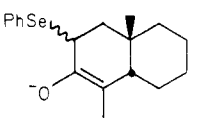

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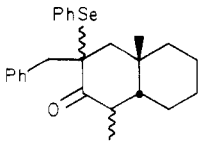
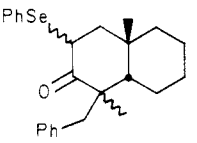
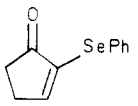


31

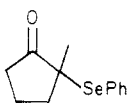


32

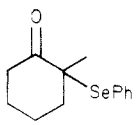
Finally, in the course of our studies we have found two α-phenylselenyl ketones which do not undergo the α,α' rearrangement. These are **33** and **34**. The only obvious



28



33



difference between these compounds and the ones given in Table I is that **33** and **34** lack any buttressing alkyl substituents. If this is indeed the reason for differences in reactivity between these compounds and the ones given in Table I, then the implication is that steric crowding at or around the α-carbon atom accelerates the α,α' rearrangement and may, in fact, be necessary for this process to be successful. Further studies involving both the synthetic and mechanistic aspects of this rearrangement will be the subject of future reports.

Acknowledgment. This work was supported by a grant from the National Institutes of Health.

Registry No. *cis*-**1**, 73825-08-8; *trans*-**1**, 73825-03-3; **2**, 80864-36-4; *cis*-**3**, 80864-37-5; *trans*-**3**, 80864-38-6; **7**, 80864-39-7; **8**, 80864-40-0; **9**, 24810-59-1; **10**, 80864-41-1; **11**, 80864-42-2; **12**, 80864-43-3; **13**, 80864-44-4; **14**, 80924-07-8; **15**, 78763-80-1; **16**, 80864-45-5; **17**, 80864-46-6; **18**, 80864-47-7; **19**, 80864-48-8; **20**, 80864-49-9; **21**, 80864-50-2; **22**, 80864-51-3; **23**, 80864-52-4; **24**, 80864-53-5; **31**, 80864-54-6; **33**, 80864-55-7; **34**, 65979-78-4.

Supplementary Material Available: Complete experimental details for all the reaction presented here (8 pages). Ordering information is given on any current masthead page.

(11) Fellow of the Alfred P. Sloan Foundation, 1980-1984. Recipient of a Camille and Henry Dreyfus Teacher-Scholar Fellowship, 1981-1986.

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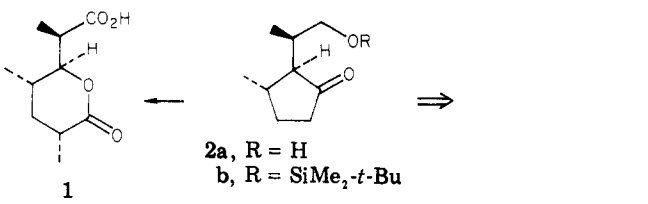
Received September 18, 1981

Synthesis of Racemic Prelog-Djerassi Lactone via a Regio- and Diastereoselective Ene Reaction†

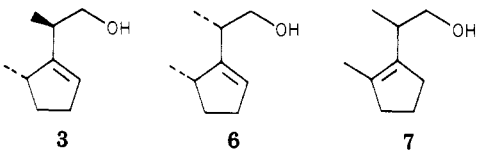
Summary: Examination of the regio- and stereochemical outcome of the ene reaction of 1-ethylidene-2-methylcyclopentanes with formaldehyde and the application to a synthesis of (±) Prelog-Djerassi lactone is described.

Scheme I

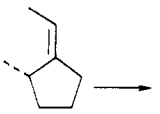


1 2a, R = H b, R = $SiMe_2$-*t*-Bu 3 4

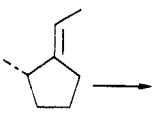
Scheme II



3 6 7



4 86:10:4



5 5:7:88 mixture of **3**, **6**, and **7**

Sir: The Prelog-Djerassi lactonic acid **1**, a degradation product of the macrolide antibiotics methymycin and narbomycin,[1] has attracted attention not only for its novel structure possessing four chiral centers but also because of its potential utility in the construction of more complex natural products.[2] A number of highly imaginative solutions to the problem of its synthesis have already appeared.[3]

Our own strategy evolved from a desire to gain some insight on the contribution of structural features to the very high stereoselectivity of the ene reaction with formaldehyde observed in our previous work regarding the generation of steroidal side chains bearing the natural C-20

(1) (a) Isolation from narbomycin degradation: Anliker, R.; Dvornik, D.; Gubler, K.; Heusser, H.; Prelog, V. *Helv. Chim. Acta* **1956**, *39*, 1785. (b) Isolation from methymycin degradation: Djerassi, C.; Zderic, J. A. *J. Am. Chem. Soc.* **1956**, *78*, 6390. (c) Final structure revision: Richards, R. W.; Smith, R. M. *Tetrahedron Lett.* **1970**, 1025. Manwaring, D. G.; Rickards, R. W.; Smith, R. M. *Ibid.* **1970**, 1029.

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