72 h. Concentration left 33.1 g of light oil, which, by VPC (5 ft × 1/8 in. 5% SE-30, 150 °C), was a mixture of two components (1.7 and 3.6 min). The oil was distilled at reduced pressure in six fractions. Fractions 1–3 yielded 13.8 g (28%) of pure methyl *N*-(2-chloroethyl)-*N*-ethylcarbamate (**10**): bp 125 °C (33 mm); IR 1705 (C=O) cm^{-1}; NMR ($CDCl_3$) δ 3.70 (s, 3, OCH_3), 3.70–3.54 (m, 4, CH_2CH_2), 3.40 (q, J = 7 Hz, 2, CH_2CH_3), 1.13 (t, J = 7 Hz, 3, CH_2CH_3).

Anal. Calcd for $C_6H_{12}ClNO_2$: C, 43.51; H, 7.30; N, 8.46. Found: C, 43.62; H, 7.28; N, 8.50.

Fractions 5 and 6 contained 17.7 g (51%) of pure 3-ethyl-2-oxazolidinone (**9**): bp 148 °C (25 mm) [lit.[9] bp 92 °C (1 mm)]; IR 1750 (C=O) cm^{-1}; NMR ($CDCl_3$) δ 4.50–4.13 (m, 2, OCH_2), 3.80–3.39 (m, 2, NCH_2CH_2), 3.30 (q, J = 7 Hz, 2, CH_2CH_3), 1.15 (t, J = 7 Hz, 3, CH_3).

Anal. Calcd for $C_5H_9NO_2$: C, 52.16; H, 7.88; N, 12.17. Found: C, 52.20; H, 7.70; N, 12.02.

Preparation of Methyl *N*-Ethyl-*N*-[2-(4-morpholinyl)-ethyl]carbamate (6). A. From 5. To a solution of 11.0 g (50.0 mmol) of **5** (prepared as in part A or C) in 50 mL of methanol was added 15 mL of 25% methanolic sodium methoxide. A white precipitate formed immediately. The mixture was concentrated and partitioned between water and methylene chloride, and the organic phase was dried (Na_2SO_4) and concentrated to leave 10.7 g (99%) of **6**: bp 111 °C (0.7 mm); IR (neat) 1705 (C=O) cm^{-1}; NMR ($CDCl_3$) δ 3.64–3.48 (m, 7, both carbamate NCH_2 groups and OCH_3, with OCH_3 s at 3.57), 3.22 (q, J = 7 Hz, 4, CH_2OCH_2), 2.60–2.27 (m, 6, three CH_2 groups adjacent to morpholino N), 1.10 (t, J = 7 Hz, 3, CH_2CH_3); mass spectrum (70 eV), m/e 216 (molecular ion).

Anal. Calcd for $C_{10}H_{20}N_2O_3$: C, 55.53; H, 9.32; N, 12.95. Found: C, 55.48; H, 9.32; N, 13.09.

B. From 10 and Morpholine. A solution of 7.42 g (44.8 mmol) of **10** and 15.7 g (180 mmol) of morpholine in 50 mL of benzene was heated at reflux for 100 h. The mixture was cooled, washed with water, dried (Na_2SO_4), and concentrated. Distillation at reduced pressure gave 8.54 g (88%) of **6**, which was identical in all respects with the material prepared as in part A.

Ethyl *N*-Ethyl-*N*-[2-(4-morpholinyl)ethyl]carbamate (7). Carbamate **7** was prepared from **5** and ethanolic sodium ethoxide, by using the procedure described for **6**: 82% yield; bp 122 °C (1.7 mm); IR 1700 (C=O) cm^{-1}; NMR ($CDCl_3$) δ 4.07 (q, J = 7 Hz, 2, OCH_2CH_3), 3.77–3.48 (m, 4, both carbamate NCH_2 groups), 3.27 (q, J = 7 Hz, 4, CH_2OCH_2), 2.60–2.27 (m, 6, three CH_2 groups adjacent to morpholino N), 1.22 (t, J = 7 Hz, 3, OCH_2CH_3), and 1.09 (t, J = 7 Hz, 3, NCH_2CH_3); mass spectrum (70 eV) m/e 230 (molecular ion).

Anal. Calcd for $C_{11}H_{22}N_2O_3$: C, 57.36; H, 9.63; N, 12.17. Found: C, 57.58; H, 9.75; N, 12.38.

4-Oxo-4*H*-1-benzopyran-2-carbonyl Chloride (11). To a slurry of 19.0 g (0.100 mol) of 4-oxo-4*H*-1-benzopyran-2-carboxylic acid[10] in 250 mL of cyclohexane was added 23.0 g (0.110 mol) of phosphorus pentachloride. After 45 min at reflux, a clear solution resulted. The solution was kept cold for 15 h, and the resulting needles were collected to yield 18.6 g (89%) of **11**: mp 104–108 °C (lit.[12] mp 108–109 °C); IR 1750 (acid chloride C=O), 1645 (ketone C=O), 1610 (C=C) cm^{-1}.

2-[*N*-Ethyl-*N*-(4-morpholinylcarbonyl)amino]ethyl 4-Oxo-4*H*-1-benzopyran-2-carboxylate (12). To a solution of 10.5 g (50.3 mmol) of **11** in 50 mL of methylene chloride was added 10.1 g (50.3 mmol) of **3**. After being stirred for 15 min the solution was washed with saturated $NaHCO_3$, dried (Na_2SO_4), and concentrated to yield 18.1 g (96%) of **12** as a viscous oil. Trituration with ether produced a white solid: mp 118–119 °C (ethanol); IR 1740 (C=O) cm^{-1}; NMR ($CDCl_3$) δ 8.34–8.10 (m, 1, aromatic), 7.95–7.30 (m, 3, aromatic), 7.07 (s, 1, H at the 3-position of benzopyranone), 4.57 (t, J = 5.5 Hz, 2, CO_2CH_2), 3.87–3.04 (m, 12, morpholinyl plus CH_2NCH_2), 1.22 (t, J = 7 Hz, 3, CH_3).

Anal. Calcd for $C_{19}H_{22}N_2O_6$: C, 60.95; H, 5.92; N, 7.48. Found: C, 60.77; H, 5.91; N, 7.42.

Compounds 13a–d, 14a–d, and 15a–d. Ureas **13a–d** were made in the same fashion as **3**. Treatment of these ureas with **11** in methylene chloride followed by workup produced, initially, the respective esters **14a–d** as oils. The gradual conversion of these oils to their corresponding acylammonium carboxylate salts **15a–d** was monitored spectrally. In the infrared spectra, the ester carbonyl bands at 1740 cm^{-1} diminished as the carbonyl bands of the inner salts at 1800 cm^{-1} intensified. When monitored by NMR, the conversions were clearly observed at δ 7.1, where one sharp signal (due to the proton at the 3-position of the benzopyranone moiety) replaced another.

Registry No. **1**, 15159-40-7; **2**, 110-73-6; **3**, 72275-32-2; **5**, 72275-33-3; **6**, 72275-34-4; **7**, 72275-35-5; **8**, 72275-36-6; **9**, 5261-18-7; **10**, 72275-37-7; **11**, 5112-47-0; **12**, 72275-38-8; **13a**, 72275-39-9; **13b**, 72275-40-2; **13c**, 72275-41-3; **13d**, 72275-42-4; **14a**, 72275-43-5; **14b**, 72275-44-6; **14c**, 72275-45-7; **14d**, 72275-46-8; **15a**, 72275-49-1; **15b**, 72275-51-5; **15c**, 72275-53-7; **15d**, 72275-55-9; *N*-ethylaziridine, 1072-45-3; methyl chloroformate, 79-22-1; morpholine, 110-91-8; 4-oxo-4*H*-1-benzopyran-2-carboxylic acid, 4940-39-0.

(9) A. H. Homeyer, U.S. Patent 2 399 118, Apr 23, 1946; *Chem. Abstr.*, **40**, 4085[3] (1946).
(10) This acid was prepared using the procedure of B. Barker and G. P. Ellis, *J. Chem. Soc. C*, 2609 (1970): mp 251–252 °C (lit.[11] mp 250 °C).
(11) V. A. Zagorevskii and D. A. Zykov, *Zh. Obshch. Khim.*, **33**, 2469 (1963); *Chem. Abstr.*, **59**, 15214*b* (1963).
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Preparation and Determination of Configurationally Pure *trans*-(2*S*,3*S*)-2,3-Epoxybutane

Volker Schurig,* Bernhard Koppenhoefer, and Waldemar Buerkle

Institut für Organische Chemie, Universität Tübingen, D 74 Tübingen, Federal Republic of Germany

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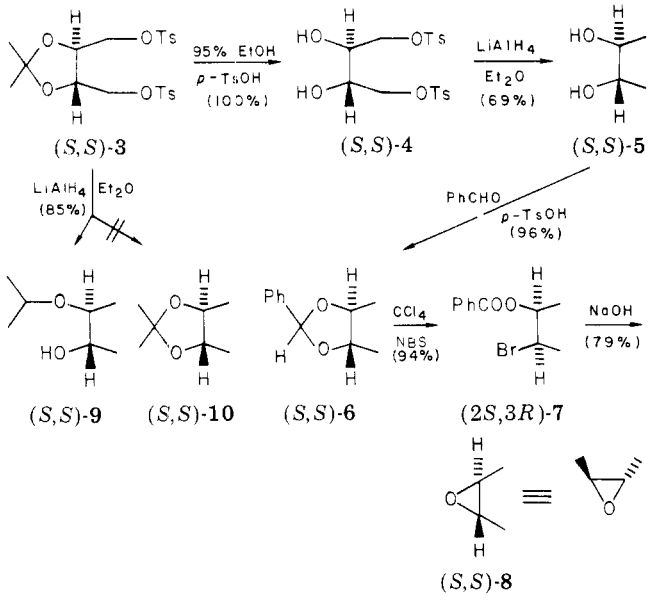
The unambiguous determination of enantiomeric compositions and absolute configurations of chiral oxiranes and related synthons is highly warranted in view of their importance for the preparation of optically active natural, pharmaceutical, and synthetic products.[1] Unfortunately, the former effort has until now lagged behind the synthetic approach. The traditional determination of "optical" purities in resorting to polarimetry is not always a reliable measure for enantiomeric compositions,[2] and, in addition, it requires the knowledge of the specific rotation ($[\alpha]_{max}$) of the pure enantiomer, usually not known with certainty. The characterization of enantiomeric compositions of oxiranes by NMR analysis in chiral solvents[3] or in the presence of chiral shift reagents[4] may be complicated by insufficient enantiomeric resolution and/or by spectral complexity, limiting its application for the accurate determination of the smallest amounts of enantiomeric impurities. We[5] and others[6] have recently shown that "complexation" gas chromatography may offer a high promise for the direct determination of enantiomeric compositions of volatile oxiranes and related substrates

(1) D. Seebach and H. O. Kalinowski, *Nachr. Chem. Tech.*, **24**, 415 (1976).
(2) A. Horeau, *Tetrahedron Lett.*, 3121 (1969).
(3) Pirkle's method; see: I. Moretti, F. Taddei, G. Torre, and N. Spassky, *J. Chem. Soc., Chem. Commun.*, 25 (1973).
(4) Whitesides' method; see: R. R. Fraser, M. A. Petit, and J. K. Saunders, *J. Chem. Soc., Chem. Commun.*, 1450 (1971); M. Kainosho, K. Ajisaka, W. H. Pirkle, and S. D. Beare, *J. Am. Chem. Soc.*, **94**, 5924 (1972); J. Gombos, E. Haslinger, and U. Schmidt, *Chem. Ber.*, **109**, 2645 (1976); B. Seuring and D. Seebach, *Helv. Chim. Acta*, **60**, 1175 (1977); J. J. Baldwin, A. W. Raab, K. Mensler, B. H. Arison, and D. E. McClure, *J. Org. Chem.*, **43**, 4876 (1978).
(5) V. Schurig, *Angew. Chem., Int. Ed. Engl.*, **16**, 110 (1977); V. Schurig and W. Bürkle, *ibid.*, **17**, 132 (1978).
(6) B. T. Golding, P. J. Sellars, and A. K. Wong, *J. Chem. Soc., Chem. Commun.*, 570 (1977).

0022-3263/80/1945-0538$01.00/0

Scheme I



by their quantitative[5] resolution on optically active metal coordination compounds used as enantioselective complexing stationary phases. Although this approach is only at the beginning of its full exploitation, significant applications are already evident.[7]

As is most important for practical purposes, no isolation, purification, and/or derivatization of substrate is required, and minute quantities of sample (i.e., 10^{-8} g of vapor) suffice for analysis. Furthermore, even traces of enantiomeric contaminants (i.e., less than 0.1%)[8] may readily be detected by the chromatographic method. Thus, for volatile substrates resolvable by GLC, the approach bears significant advantages over the use of NMR spectroscopy for evaluating absolute enantiomeric compositions.

Here we wish to report on the stereochemistry of aliphatic oxirane formations, previously carried out in the literature, by measuring their correct configurational compositions employing complexation chromatography on optically active nickel(II) bis[(1*R*)-3-(heptafluorobutyryl)camphorate] (**1**).[7]

trans-(2*S*,3*S*)-2,3-Epoxybutane (**8**) has been prepared in eight steps (total yield: 39%) by "chiral pool" synthesis[1] from (2*R*,3*R*)-tartaric acid (**2**). The synthetic scheme modeled on literature procedures (Scheme I) is straightforward and suitable for large-scale preparation. The novel $LiAlH_4$ reduction of the free diol (2*S*,3*S*)-1,4-di-*O*-tosylthreitol (**4**), which is readily available from (2*S*,3*S*)-1,4-di-*O*-tosyl-2,3-*O*-isopropylidenethreitol (**3**),[9] affords *threo*-(2*S*,3*S*)-2,3-butanediol (**5**) in a very pure state. It should be noted that $LiAlH_4$ reduction of the *protected* diol **3** does not yield *threo*-(2*S*,3*S*)-2,3-*O*-isopropylidenebutanediol (**10**), as reported for the corresponding 1,4-di-*O*-mesyl-2,3-*O*-isopropylidenethreitol,[10] but a new compound, i.e., *threo*-(2*S*,3*S*)-3-isopropyloxy-2-butanol (**9**). The strategy devised in the literature to obtain dissymmetric (C_2 point group) *trans*-(2*R*,3*R*)-2,3-epoxybutane (**8**) involves two consecutive inversions at one of the equivalent asymmetric carbon atoms of *threo*-(2*R*,3*R*)-2,3-butanediol.[11]

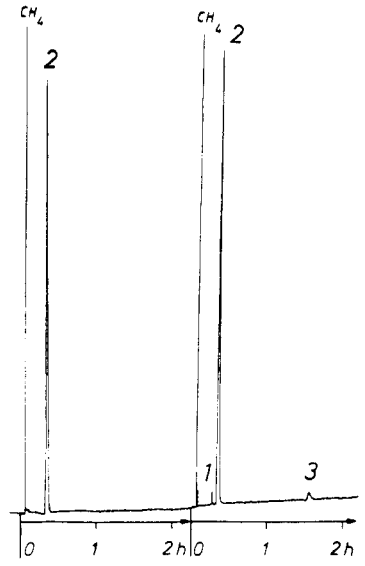


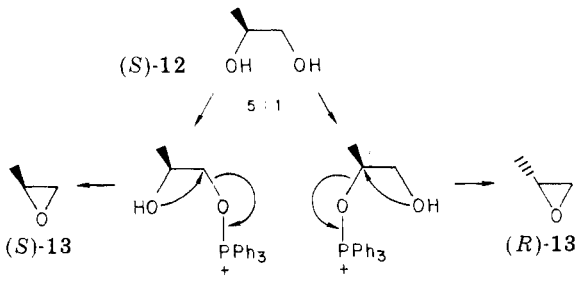
Figure 1. Determination of the diastereomeric and enantiomeric purity of (2*S*,3*S*)-2,3-epoxybutane (**8**) by complexation gas chromatography on nickel(II) bis[(1*R*)-3-(heptafluorobutyryl)-camphorate] (**1**) in squalane at 70 °C: (left) (2*S*,3*S*)-**8** prepared according to Scheme I, purity >99.9%; (right) (2*S*,3*S*)-**8** with trace amounts of racemic **8** and cis-**11**. Assignment: *trans*-(2*R*,3*R*)-2,3-epoxybutane (**1**), *trans*-(2*S*,3*S*)-2,3-epoxybutane (**2**), *cis*-2,3-epoxybutane (**3**).

We have prepared *trans*-(2*S*,3*S*)-2,3-epoxybutane (**8**) from *threo*-(2*S*,3*S*)-2,3-butanediol (**5**) following the general procedure of Seeley and McElwee.[12] Complexation chromatography of the epoxide on nickel(II) bis[(1*R*)-(3-heptafluorobutyryl)camphorate] (**1**)[7] revealed that **8** was at least 99.9%(!) diastereomerically and enantiomerically pure (cf. Figure 1). Since only distillative workup was involved, complete loss of any meso diastereomer formed by epimerization appears unlikely. The *diastereomeric* purity of **8** then implies that the transfer of **5** to **8** proceeds with complete stereospecificity as noted previously for the cis diastereomer **11**.[12] This result is also corroborated by the clean NMR spectra of **8** and the intermediates **5**–**7**. Since it has been shown that no appreciable separation of enantiomers should occur during the phase transition liquid–gaseous,[13] the *enantiomeric* purity of **8** proves the absence of double racemization leading to (2*R*,3*R*)-**8**, and it implies that all liquid precursors, including the key diol (2*S*,3*S*)-**5**, were also enantiomerically pure. We are therefore able to assign the correct specific rotation ($[\alpha]_{max}$) for *trans*-(2*S*,3*S*)-2,3-epoxybutane (**8**), i.e., $[\alpha]^{25}_D$ −58.8° (neat),[14] and for *threo*-(2*S*,3*S*)-2,3-butanediol (**5**), i.e., $[\alpha]^{25}_D$ +13.38° (neat),[16] as well as for all synthetic intermediates

(7) V. Schurig, B. Koppenhöfer, and W. Bürkle, *Angew. Chem., Int. Ed. Engl.*, **17**, 937 (1978).
(8) E. Gil-Av, *J. Mol. Evol.*, **6**, 131 (1975).
(9) W. Dumont, J.-C. Poulin, T.-P. Dang, and H. B. Kagan, *J. Am. Chem. Soc.*, **95**, 8295 (1973).
(10) J. J. Plattner and H. Rapoport, *J. Am. Chem. Soc.*, **93**, 1758 (1971). The reported isolation of pure **5** after hydrolysis is difficult.[20a]

(11) (a) H. J. Lucas and H. K. Garner, *J. Am. Chem. Soc.*, **70**, 990 (1948). (b) M. S. Newman and C. H. Chen, *J. Org. Chem.*, **38**, 1173 (1973). (c) M. S. Newman and D. R. Olson, *ibid.*, **38**, 4203 (1973).
(12) D. A. Seeley and J. McElwee, *J. Org. Chem.*, **38**, 1691 (1973).
(13) J.-P. Guetté, D. Boucherot, and A. Horeau, *Tetrahedron Lett.*, 465 (1973).
(14) Thus, the values reported by Lucas and Garner,[11a] i.e., $[\alpha]^{25}_D$ 58.65 and 59.05°, are confirmed. Lower figures reported[11c,15a] obviously correspond to preparations of lower enantiomeric purities. Data in various solvents[15b] permit no direct comparison.
(15) (a) W. Kirmse, H.-J. Ratajczak, and G. Rauleder, *Chem. Ber.*, **110**, 2290 (1977); (b) K. Mori, S. Tamada, and M. Matsui, *Tetrahedron Lett.*, 901 (1978).
(16) At present there is no method available for the direct determination of the enantiomeric purity of **5**. Our figure for configurationally pure (2*S*,3*S*)-2,3-butanediol (**5**) agrees with that of Neish.[17a] It should be noted that (2*R*,3*R*)-**5** obtained by microbial synthesis with *Bacillus polymyxa* obviously does not always furnish enantiomerically pure diol as judged from the reported specific rotations, i.e., $[\alpha]^{25}_D$ = −12.1°,[17b] −11.14°.[17c] The highest reported figure for **5**, i.e., α_D −14.1°, appears to be erroneous.[17d]

Scheme II



(see Experimental Section).

Having configurationally pure *threo*-(2*S*,3*S*)-2,3-butanediol (**5**) at hand, we reinvestigated the stereochemistry of the conversion of **5** to **8** via *threo*-(2*S*,3*S*)-2,3-diacetoxybutane and *erythro*-(2*S*,3*R*)-3-chlorobutanol according to the procedure of Lucas and Garner[11a] and via (2*S*,3*S*)-2-carboxy-2,4,5-trimethyl-1,3-dioxolane and *erythro*-(2*S*,3*R*)-3-chloro-2-butyl acetate according to Newman and Chen,[11b] respectively. We could confirm that both reactions proceed with complete stereospecificity. Thus, in all three reactions a common step, namely the stereospecific back-side attack of the halogenide ion on one of the asymmetric carbon atoms of a cyclic intermediate[18] is operative.

We have also investigated the stereochemical course of a novel "one-pot" reaction to convert 1,2-diols into 1,2-epoxides by employing the combined reagents triphenylphosphine/diethyl azodicarboxylate.[19] Thus, by complexation chromatography we found that only inactive *cis*-2,3-epoxybutane (**11**) but neither one of the trans enantiomers **8** was formed from pure *threo*-(2*S*,3*S*)-2,3-butanediol (**5**), establishing complete Walden inversion at either one of the equivalent asymmetric carbon atoms of **5**. Under the same conditions (i.e., 25 °C, benzene) the conversion of (*S*)-1,2-propanediol (**12**), containing less than 1.8% *R* enantiomer,[7] yielded predominantly (*S*)-1,2-epoxypropane (**13**) (67% ee by complexation chromatography).[7] Assuming the same mechanism, i.e., complete Walden inversion, holds, the peak ratio observed for **13** (*S*:*R* = 5:1) is then an approximate measure for the steric course of the reaction, namely the preferential regioselective attack of phosphorus at the sterically less hindered primary hydroxyl group of **12** (cf. Scheme II).

Experimental Section

Instrumentation. ^{1}H PFT NMR spectra were recorded on a Bruker WH 90 (frequency 90 MHz) spectrometer. ^{13}C NMR spectra were recorded on a Bruker HFX 90 (frequency 20.115 MHz) spectrometer (δ values are given in parts per million from Me_4Si. Mass spectra were recorded on a Varian-MAT 711 spectrometer. Specific rotations were recorded with a Perkin-Elmer 141 polarimeter using a thermostated 1-dm cell. Complexation gas chromatography was carried out on a Carlo-Erba Fractovap 2101 instrument, provided with an externally heated (120 °C) flame ionization detector. A 100 m × 0.5 mm nickel capillary column (Handy and Harmon Tube Co., Norristown, PA) was coated with 0.1 *m* nickel(II) bis[(1*R*)-3-(heptafluorobutyryl)camphorate] in squalane.[7] Oxiranes were injected by a "head-space" technique, i.e., as air-diluted vapor using a 10-μL gas-tight syringe; split ratio 1/50; flow 3.8 mL of nitrogen min^{-1}.

Materials. Caution: The necessary care when working with alkylating oxiranes should be observed.

(2*S*,3*S*)-1,4-Di-*O*-tosyl-2,3-*O*-isopropylidenethreitol (3). Synthesis of **3** (948 g) was accomplished in four runs from (2*R*,3*R*)-tartaric acid (Merck Co.) via (2*R*,3*R*)-dimethyl 2,3-*O*-isopropylidenetartrate and (2*R*,3*R*)-2,3-di-*O*-isopropylidenethreitol:[20] total yield 79%; mp 92 °C (uncor.); $[\alpha]^{22}_D$ -12.3° (*c* 4.2, $CHCl_3$).

(2*S*,3*S*)-1,4-Di-*O*-tosylthreitol (4). (2*S*,3*S*)-**3** (600 g, 1.275 mol) and *p*-toluenesulfonic acid (3 g) were refluxed in 3 L of ethanol and 50 mL of water. The solvent was gradually removed (1 mL/min) by distillation employing an efficient column. The temperature at the top of the column rose from 60 to 77 °C within 16 h. The concentrated residue was recrystallized from $CHCl_3$ to give 550 g of **4** (nearly quantitative): mp 76–77 °C (uncor); $[\alpha]^{20}_D$ -4.6° (*c* 2.1, acetone) (lit.[9] $[\alpha]^{20}_D$ +4.6° (*c* 2, acetone) for the 2*R*,3*R* isomer).

***threo*-(2*S*,3*S*)-2,3-Butanediol (5).** The flask of a Soxhlet extraction apparatus was carefully charged with 25 g (0.66 mol) of $LiAlH_4$ in 1 L of diethyl ether under dry N_2, whereas the thimble was filled with 112.5 g (0.261 mol) of (2*S*,3*S*)-**4**. Continuous extraction by reflux was maintained for 48 h. The reaction mixture was cooled to 0 °C, and after successive cautious additions of water (20 mL) and 2 N NaOH (20 mL), stirring was continued for 2 h. The white precipitate was removed by filtration and extracted thoroughly with ether (Soxhlet). The combined ethereal extracts were dried (Na_2SO_4), concentrated, and distilled at reduced pressure: yield 16.2 g (69%) (mean from four preparations); bp 75 °C (10 mm); α^{25}_D +13.19° (neat), d^{25}_4 0.9869,[11a] $[\alpha]^{25}_D$ +13.37°, organic impurities <0.5% by GLC (SE 30, 20-m glass capillary, deactivated with $BaCO_3$). For the purpose of determining the correct specific rotation, **5** was azeotropically fractionated with benzene for 16 h to remove water and organic contaminants: $[\alpha]^{25}$ (neat) +13.38° (D), +13.97° (578), +15.79° (546), +25.97° (436), +38.76° (395) (GLC purity, 99.97%); ^{13}C NMR ($CDCl_3$) δ 72.0 (C2, C3), 18.9 (C1, C4). The spectrum showed no absorptions for the meso diastereomer (δ 70.6, 16.6).

(2*S*,3*S*)-4,5-Dimethyl-2-phenyl-1,3-dioxolane (6). Freshly distilled benzaldehyde (40.4 g, 0.380 mol), 33.8 g (0.375 mol) of (2*S*,3*S*)-**5**, and 0.2 g of *p*-toluenesulfonic acid were refluxed in 130 mL of benzene employing a water separator for 8 h. After addition of 0.2 g of Na_2CO_3, the mixture was fractionated at reduced pressure to give 64.2 g of **6** (96%): bp 103 °C (10 mm); α^{20}_D +28.78° (neat), d^{20}_4 1.031, $[\alpha]^{20}_D$ +27.91° (neat). The ^{1}H NMR spectrum ($CDCl_3$) showed no presence of diastereomers.[21] ^{13}C NMR ($CDCl_3$) δ 138.7, 128.9, 128.2, 126.4, 102.6, 80.2, 78.5, 17.1, 16.8.

***erythro*-(2*S*,3*R*)-3-Bromo-2-butyl Benzoate (7).** Following the literature procedure,[12] we treated 63 g (0.354 mol) of (2*S*,3*S*)-**6** with 63 g (0.354 mol) of *N*-bromosuccinimide. The crude product was distilled at reduced pressure: bp 88 °C (0.06 mm); 85.9 g of **7** (94.4%); α^{20}_D +5.58° (neat), d^{20}_4 1.324, $[\alpha]^{20}_D$ +4.21° (neat); ^{13}C NMR ($CDCl_3$) δ 165.6, 133.1, 130.3, 129.8, 73.6, 51.7, 21.7, 16.6.

***trans*-(2*S*,3*S*)-Epoxybutane (8).** A mixture of 84.8 g (0.330 mol) of (2*S*,3*R*)-**7** and 30.0 g of NaOH in 250 mL of diethylene glycol, vigorously stirred at 120 °C, afforded 18.8 g (79%) of **8**, which was collected in a -70 °C trap (Hg valve) at reduced pressure and redistilled over KOH pellets: α^{25}_D -47.02° (neat), d^{25}_4 0.7998,[11a] $[\alpha]^{25}$ -58,8° (D), -61.0° (578), -68.3° (546), -108° (436, 1-cm cell), -151° (365, 1-cm cell) (neat); ^{13}C NMR ($CDCl_3$) δ 55.0 (C2, C3), 17.0 (C1, C4).

***threo*-(2*S*,3*S*)-3-(2-Propyloxy)-2-butanol (9).** A suspension of 141 g (0.30 mol) of (2*S*,3*S*)-**3** in 200 mL of diethyl ether was slowly added to 45 g (1.2 mol) of $LiAlH_4$ in 1 L of diethyl ether under dry N_2. The mixture was refluxed for 24 h and worked up as **5**. Fractional distillation afforded the following: 33.5 g of **9** (84.5%); bp 143–144 °C (728 mm); α^{20}_D +37.64° (neat); purity >99.8% by GLC (OV 1 on Chromosorb P AW-DMCS); mass spectrum (as the trimethylsilyl derivative, obtained with bis(trimethylsilyl)trifluoracetamide in CH_2Cl_2, 1 h, 25 °C) *m/e* 189 (M - 15); IR (film) 3400, 2900, 1450, 1380, 1285, 1265, 1100, 1025, 920, 880 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 77.8 (C2), 70.9, 69.8 (C3 and C1′), 23.6, 22.1 (C2′ and C2″), 18.5 (C4), 16.4 (C1); the diaste-

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reotopic methyl groups C2′ and C2″ were split by 1.5 ppm. Anal. Calcd for $C_7H_{16}O_2$: C, 63.60; H, 12.20. Found: C, 64.06; H, 12.38.

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Sila- and Germacyclopentan-2-ones from Metallated Enol Ethers[1a]

John A. Soderquist*

Department of Chemistry, University of San Francisco, San Francisco, California 94117

Alfred Hassner*

Department of Chemistry, State University of New York, Binghamton, New York 13901

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We wish to report the synthesis of the novel sila- and germacyclopentan-2-one systems (3) using the reaction sequence outlined in Scheme I. These compounds represent the smallest known cyclic acylsilane[2,3] and the first cyclic acylgermane. Larger silicon-containing ring systems have been prepared using the dithiane route.[4] However, this method fails in the hydrolysis step for the 1-silacyclopentan-2-one case.

The reaction sequence shown in Scheme I illustrates several important new features which warrant mention. For one, the formation of 1 from *trans*-1-methoxybutadiene indicates for the first time that this compound can be metallated regio- and stereospecifically giving isolable butadienyl adducts.[5,8] The cyclization of 1 to give 2 is the first example of an intramolecular hydrosilylation or hydrogermylation in which a functionalized ring system is formed. Previous attempts to obtain silacycloalkanes with masked ketone functionality using this approach failed to give the cyclic product.[6] Other 2-functionalized

Scheme I

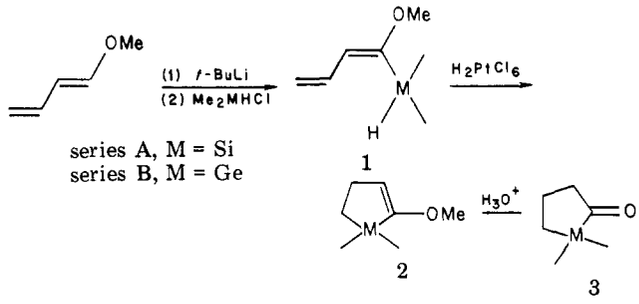

Table I. Spectroscopic Properties of the Carbonyl Moiety in Metallacyclopentan-2-ones[a]

			
UV, nm[b]	299 (20)	398 (108)	387 (130)
^{13}C NMR, ppm[c]	217.2	258.3	250.5
IR, cm^{-1}	1745	1674	1672

[a] Values for cyclopentanone were taken from ref 20. Neat films were used for the IR analysis, whereas $CDCl_3$ and C_6H_{14} were used as solvents for the ^{13}C NMR and UV studies, respectively. The cited UV absorbance is the most intense band of five juxtaposed peaks. [b] The molar extinction coefficient follows λ_{max} in parentheses. [c] For the C=O carbon.[12]

silacyclopentanes are presently available only by very tedious and circuitous routes.[7] Finally, the formation of 3 from 2 in good yield illustrates the utility of enol ethers as metallated ketone precursors. In fact, we found this method to constitute a general synthesis of acyl silanes, germanes, and stannanes from lithiated vinyl ethers.[1a,8,11]

Metallation of *trans*-1-methoxybutadiene was accomplished by treating a THF solution of this compound at −78 °C with an equimolar amount of *tert*-butyllithium in pentane followed by a slow warm-up to −20 °C. Treatment of the lithium compounds with an equimolar amount of the chlorodimethylsilane (or germane) in pentane at −78 °C gave the desired butadienyl adducts (1) as the *Z* isomers exclusively in 70–80% yield. Cyclization of 1 was accomplished in benzene solution at reflux temperature for **1A** or at 160 °C for the neat **1B** using 0.3 mol% chloroplatinic acid catalysis. Yields of 20–30% were routinely obtained. Attempts to improve on this value by varying the conditions and catalyst were unsuccessful. Acid-catalyzed hydrolysis of 2 proceeds cleanly at 25 °C in aqueous acetone to give the ketones 3 in 50–60% isolated yields.

The spectroscopic properties of the yellow-green metallacyclopentan-2-ones (3) are given in Table I. These data clearly show the important spectroscopic differences between these metalloidal carbonyl derivatives and cyclopentanone. The n → π* band[3,9] in **3A** (at 398 nm) is slightly shifted, as expected,[10] from the corresponding silacyclohexan-2-one system[3] (at 380 nm).

The ^{13}C NMR downfield carbonyl absorbance of **3A** relative to cyclopentanone agrees well with spectra of the acyclic ketone counterparts.[8,11,12] The ^{1}H NMR spectra of 3 were consistent with the assigned structures. Additional supportive information was obtained by using a

(1) (a) This paper is part 3 of Vinylmetalloids. For part 2, see J. A. Soderquist and A. Hassner, *J. Organomet. Chem.*, **156**, C12 (1978); see also A. Hassner and J. A. Soderquist, *ibid.*, **131**, C1 (1977).

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(9) In 95% ethanol **3A** shows λ_{max} 396.5 nm (ε 100). This absorbance has also been interpreted in terms of a $\sigma \rightarrow \pi^*$ transition [B. G. Ramsey, A. G. Brook, A. R. Bassindale, and H. Bock, *J. Organomet. Chem.*, **74**, C41 (1974)].

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(12) For instance, absorbances at 48.8, 19.6 and 13.1 ppm were observed for the ring carbons at positions 3, 4, and 5, respectively. The methyl groups on silicon were found at −5.7 ppm. For **3B**, similar values were observed at 48.1, 21.3, 14.7 and −5.0 ppm, respectively.

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