thiocyanate salt could be precipitated out by the addition of sodium thiocyanate to a concentrated solution of the product in wet methanol.[7] Preparation of macrocrystalline material was difficult because of the hygroscopic nature of the various salts tried.

This photoproduct is evidently the O-bonded isomer, $Co(en)_2[OS(O)CH_2CH_2NH_2]^{2+}$, designated as CoOSON. The chromatographic elution rate is that for a divalent ion, and is independent of pH over the range 2–8.7. Further, the visible–UV absorption spectrum of an irradiated solution of CoSOON is also independent of pH in this range. Thus, neither complete aquation to give free ligand $NH_2CH_2CH_2SO_2^-$, nor partial aquation to give $Co(en)_2(NH_2CH_2CH_2SO_2)(H_2O)^{2+}$ could have occurred. Confirmation that the photoproduct is the O-bonded isomer comes from the absorption spectrum. The position of the first ligand field absorption band of CoOSON is characteristic of a Co(III) complex having one oxygen and five nitrogens coordinated.[8] The lack of the characteristic intense charge-transfer (CT) band at ~285 nm confirms that sulfur is not coordinated,[9] but the new CT band at 326 nm indicates that the sulfinate moiety can still interact with the Co(III) center. This would be true for the O-bonded isomer, but not if the group were detached. Further, the 326-nm band (ϵ 4100 M^{-1} cm^{-1}) is analogous to an absorption feature present in the transient spectrum observed by Harris and co-workers [333 nm (ϵ ~2100 M^{-1} cm^{-1})].[4] A similar CT band is present in the spectra of other Co(III) complexes in which sulfur is separated from cobalt by one ligating atom,[10] as in a Co(III)–sulfenamide complex.[10a] We thus assign our 326-nm absorption to CT from the sulfinic acid chromophore to Co(III).

Other spectral aspects are summarized in Table I. The 100-MHz NMR spectrum of CoOSON is very similar to that of CoSOON, except that the resonance attributable to the $S-CH_2$ protons occurs significantly further upfield in the former. Interestingly, the lack of an NH_2 proton signal for CoOSON indicates that these protons are much more easily exchanged than they are in the starting complex. The latter showed NH_2 proton resonance even after several days in D_2O solution.

The vibrational data obtained from the infrared and Raman spectra of the two complexes were complicated by the large number of ligand vibrations present. Also, both complexes are poor Raman scatterers. However, the observed vibrational features not common to both product and starting complex are given in Table I. It can be seen that the strong vibration at 1190 cm^{-1}, likely due to the asymmetric O=S=O stretch,[1,3,9a] is not present in the product. In the product, two new vibrations appear, at ~1035 and 950 cm^{-1}, attributable, respectively, to the S=O stretching mode and to the asymmetric Co–O–S stretching mode of an *O*-sulfinato ligand.[1,3] Due to the overlapping C–C and C–N vibrations in the 1000–1100-cm^{-1} region, it was not possible to confirm the absence of a symmetric O=S=O stretching mode in the product spectrum. This mode occurs at 1080 cm^{-1} in CoSOON.[9a]

Chemical properties of CoOSON include the following. The aqueous (or methanolic) solution is not photosensitive in the 350–450-nm region. It does, however, revert thermally to CoSOON. The reaction is very clean and is first order. Kinetic studies over the temperature range 28–67 °C give $\Delta H^{\circ\ddagger} = 22.6$ kcal mol^{-1} and $\Delta S^{\circ\ddagger} = -15.6$ eu (corresponding to a half-life of about 600 h at room temperature). While CoOSON shows no weak acid or base properties, major spectral change does occur to the CT band in 1–8 M perchloric acid solution. There is a large blue shift, leaving a shoulder at about 270 nm. The first ligand field band maximum changes only slightly, however, from 512 to 508 nm. These spectral changes were reversible even after several days, and an acid–base equilibrium is indicated. Spectrophotometric titration with solutions buffered to ionic strength 8 M by means of sodium perchlorate gave a pK_a of -0.7 (uncorrected for H^+ activity coefficient changes). Possible protonation sites would be (a) the Co-bonded oxygen, (b) the sulfur, and (c) the S=O oxygen; case (a) seems the least likely in view of the minimal change in the ligand field band.

The photochemical generation of CoOSON, a thermodynamically unstable and perhaps otherwise unobtainable linkage isomer of CoSOON, is somewhat analogous to the nitro to nitrito linkage isomerization observed in the photolysis of $Co(NH_3)_5(NO_2)^{2+}$.[11] The mechanism may be similar, in that photochemical homolytic bond fission may occur to break the Co–S bond of CoSOON, followed by rapid cage recoordination to yield CoOSON. Unlike the case with the nitro complex, however, there is negligible redox decomposition so that the photochemical reaction is unusually clean. Current efforts are directed toward obtaining crystals of a salt of CoOSON suitable for X-ray structure determination. Finally, preliminary observations are that the behavior of the corresponding cysteinesulfinato complex on irradiation is very similar to that of CoSOON; details will be reported later.

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[7] Too slow a crystallization leads to a different red salt, which analyzes for $[Co(en)_2(NCS)_2]NCS$. Anal. Calcd: C, 23.79; N, 27.75; H, 4.56. Found: C, 23.92; N, 27.64; H, 4.52.

[8] See R. A. D. Wentworth and T. S. Piper, *Inorg. Chem.*, 4, 709 (1965).

[9] (a) B. A. Lange, K. Libson, E. Deutsch, and R. C. Elder, *Inorg. Chem.*, 15, 2985 (1976). (b) C. J. Weschler and E. Deutsch, *ibid.*, 12, 2682 (1973).

[10] (a) G. J. Gainsford, W. G. Jackson, and A. M. Sargeson, *J. Am. Chem. Soc.*, 99, 2383 (1977). (b) M. Woods, J. Karbwang, J. C. Sullivan, and E. Deutsch, *Inorg. Chem.*, 15, 1678 (1976).

[11] V. Balzani, R. Ballardini, N. Sabbatini, and L. Moggi, *Inorg. Chem.*, 7, 1308 (1968).

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Claisen Rearrangements of Lactonic (Silyl) Enolates: A New Route of Functionalized Cycloalkenes

Sir:

The Claisen rearrangement, in both its aromatic and aliphatic modes,[1,2] has been of considerable value in organic synthesis. Büchi[3] demonstrated the rearrangement of dihydropyran (**1**) to cyclohexene (**2**) under forcing conditions (ca. 400–425 °C in a flow system or 240 °C in a sealed tube). In the Ireland[4] rearrangement, **3** → **4**, a relatively accessible acyl oxygen bond is used to furnish a more difficultly available carbon–carbon bond. Moreover, the ability to generate systems such as **3** with high *E* or *Z* stereoselectivity,[4b,c] in conjunction with the chairlike geometry of the Claisen rearrangement, allows for erythro:threo stereospecificity in the formation of **4**.

We have investigated the feasibility of using vinyl lactones such as **5** as precursors of cycloalkenes (cf. **8**). Below, we report (i) that the reorganization reaction, **6** → **7**, is eminently feasible provided that $n > 1$, (ii) that an unusual, stereospecific [1,3] rearrangement occurs in constrained versions of system **6** (cf. **5k–m** → **16k–m**), (iii) that relative to the reaction **1** → **2**, the **6** → **7** rearrangement occurs under remarkably mild conditions, and (iv) that its stereochemical outcome is indicative of a boatlike transition state. See Scheme I.

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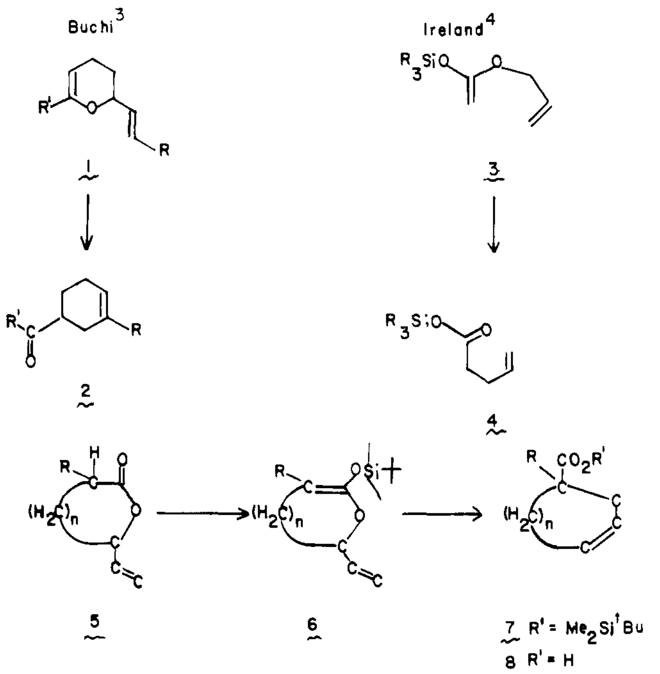
[1] Rhoads, S. J.; Raulins, N. R. *Org. React. (N.Y.)* 1975, 22, 1.

[2] Ziegler, F. E. *Acc. Chem. Res.* 1977, 10, 227.

[3] (a) Büchi, G.; Powell, J. E., Jr. *J. Am. Chem. Soc.* 1967, 89, 4559. (b) *Ibid.* 1970, 92, 3126.

[4] (a) Ireland, R. E.; Mueller, R. H. *J. Am. Chem. Soc.* 1972, 94, 5897. (b) Ireland, R. E.; Willard, A. K. *Tetrahedron Lett.* 1975, 3975. (c) Ireland, R. E.; Mueller, R. H.; Willard, A. K. *J. Am. Chem. Soc.* 1976, 98, 2868. (d) *J. Org. Chem.* 1976, 41, 986. (e) Ireland, R. E.; Thaisrivongs, S.; Wilcox, C. S. *J. Am. Chem. Soc.* 1980, 102, 1155.

Scheme I



Three routes were employed for the preparation of the required lactones (**5a–m**);[5] see Scheme II. In route (a), aldehyde ester **9** (n = 3 or 4)[6–11] reacts with a vinylic organometallic reagent. For **5a** and **5i**, "Met" was MgBr, and for **5d** and **5e** "Met" was Al(i-Bu)$_2$CH$_3$.[12] Lactonization of the derived hydroxy acids gave the required substrates, **5**. In route (b), an unsaturated aldehyde of the type **10** reacts with Grignard reagent **11**.[13–17] Acidic hydrolysis affords hemiacetal type **12**, which on oxidation[16] provides **5**. Route (c) involves the selenolactonization[18] of olefinic acids of the type **13**, to afford acids of the type **14**, which are converted to **5** in the usual way.[19] Finally, the three lactones **5c**, **e**, and **l**, bearing methyl groups α to the carbonyl centers, were prepared from their respective demethyl precursors by standard alkylation with methyl iodide.[20]

Scheme II

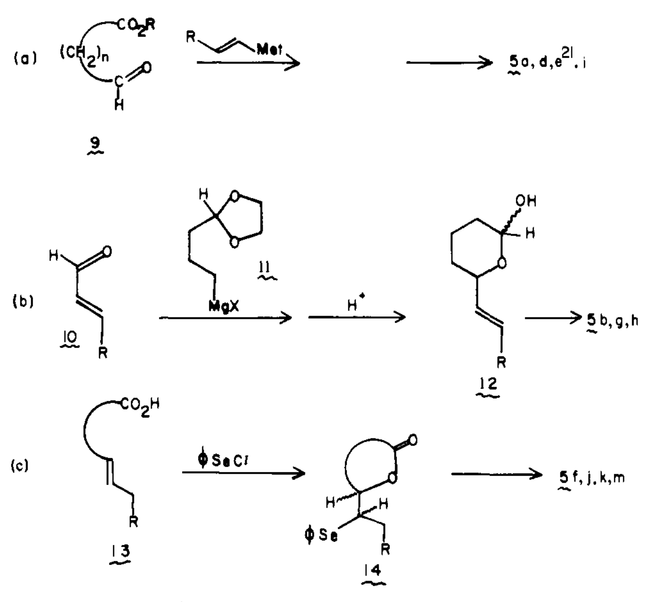
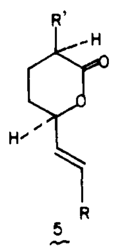
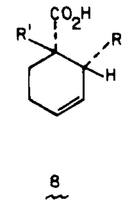
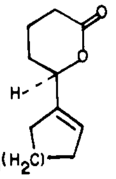
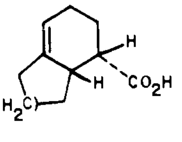
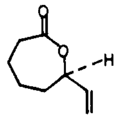
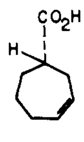
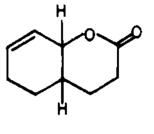
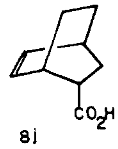


Table I

 5	a R = R' = H	63%	 8
	b R = Me; R' = H	75%	
	c R = H; R' = Me	62%	
	d R = C$_5$H$_{11}$; R' = H	89%	
	e R = Et; R' = Me	71%	
	f R = ϕ; R' = H	77%	
	g n = 1	60%	
	h n = 2	62%	
 5i	i	73%	 8i
 5j	j	44%	 8j

The required mixed ketene acetals (**6**) were obtained in a standard manner[4b,c] from the lactone enolates.[20] The rearrangements of **6a–j** were typically carried out in a 0.2 M toluene solution heated at a bath temperature of 105 °C. Progress was monitored by NMR analysis of a parallel reaction, using toluene-d_8 as the solvent. Particularly helpful in this regard was the disappearance of the Me$_2$Si resonance of **6**, typically appearing at $\delta \cong 0.17$, and its replacement by an absorption at $\delta \cong 0.23$

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[5] Satisfactory IR, NMR, and mass spectral data were obtained for these compounds.

[6] For these studies, we employed compounds **9**, n = 3 (as precursors to **5a**, **d**, and **e**) and n = 4 (as a precursor to **5i**). To prepare **5a**, **d**, and **e**, we used both the methyl ester[7] and *tert*-butyldimethyl silyl ester versions of **9**, n = 3. These were obtained by ozonolysis of the corresponding enol ethers.[8,9] The lactonizations were achieved by the reaction of trifluoroacetic acid on the corresponding hydroxy acids. While we have used this lactonization approach with good success in more substituted versions of **9**, it is not a particularly attractive method in the unsubstituted series (CH$_2$)$_n$, wherein the lactonization is far from spontaneous, and the stability of the ω-vinyl lactones to TFA and to subsequent purification on silica gel is only marginal. The overall yields in the cases reported here were in the range of 34–65%. Compound **9**, n = 4 and R = CH$_3$,[10] which served as a precursor to **5i**, was prepared in the same way.[8,9] The lactonization leading to **5i** was carried out with 2-chloro-N-methylpyridinium iodide.[11] The yield was 61%.

[7] McElvain, S. M.; McKay, G. R., Jr. *J. Am. Chem. Soc.* **1955**, *77*, 5601.

[8] Wohl, R. A. *Synthesis* **1974**, 38.

[9] Clark, R. D.; Heathcock, C. H. *Tetrahedron Lett.* **1974**, 2027.

[10] Alder, K.; von Brachel, H. *Justus Liebigs Ann. Chem.* **1962**, *651*, 141.

[11] Mukaiyama, T.; Masahiro, U.; Saigo, K. *Chem. Lett.* **1976**, 49.

[12] Zweifel, G.; Steele, R. B. *J. Am. Chem. Soc.* **1967**, *89*, 2754.

[13] This Grignard reagent was prepared from the corresponding bromoacetal[14] by reaction with magnesium in THF.[15] The yields for the addition hydrolysis sequence are in the range 55–70%. In each of the three cases, workup afforded the hemiacetal with no apparent hydroxyaldehyde.

[14] The bromoacetal was prepared via standard oxidation[16] and ketalization of the corresponding 4-bromobutan-1-ol.[17]

[15] Cf: Forbes, C. P.; Wenteler, G. L.; Wiechers, A. *J. Chem. Soc., Perkin Trans. 1* **1977**, 2353.

[16] Corey, E. J.; Suggs, J. W. *Tetrahedron Lett.* **1975**, 2647.

[17] Krüerke, U. *Chem. Ber.* **1962**, *95*, 174.

[18] Nicolaou, K. C.; Seitz, S. P.; Sipio, W. J.; Blount, J. F. *J. Am. Chem. Soc.* **1979**, *101*, 3884.

[19] Reich, H. J.; Renga, J. M.; Reich, I. L. *J. Am. Chem. Soc.* **1975**, *97*, 5434.

[20] (a) Herrmann, J. L.; Schlessinger, R. H. *J. Chem. Soc., Chem. Commun.* **1973**, 711. (b) Cregge, R. J.; Herrmann, J. L.; Lee, C. S.; Richman, J. E.; Schlessinger, R. H. *Tetrahedron Lett.* **1973**, 2425.

[21] The lactone **5e** was prepared via methylation [20] of (E)-6-(1-butenyl)-2-pyranone.

characteristic of the Me_2Si protons of the resultant ester **7**. This change correlated well with the disappearance of signals in the regions δ 3.7–3.9 and δ 4.1–4.2 associated with the vinylic and allylic ($C\mathit{H}ORCH{=}CH_2$) protons of **6**. The silyl esters were cleaved with aqueous HCl in THF. The yields provided in Table I are from the lactones **5** to the homogeneous acids **8**. This initial phase of the investigation did not involve any serious attempts at yield optimization.

Several features of the ten successful cases shown in Table I are deserving of emphasis. The temperatures (105 °C) required for rearrangement to occur in an acceptable time (30 min to 10 h)[22] are considerably lower than those required for the analogous Büchi process.[3] This is in keeping with the trend in acyclic Claisen rearrangements wherein the rate of Ireland's[4] silyl ketene acetal variation is much faster than the classical vinyl ether case,[1] for comparable substitution.

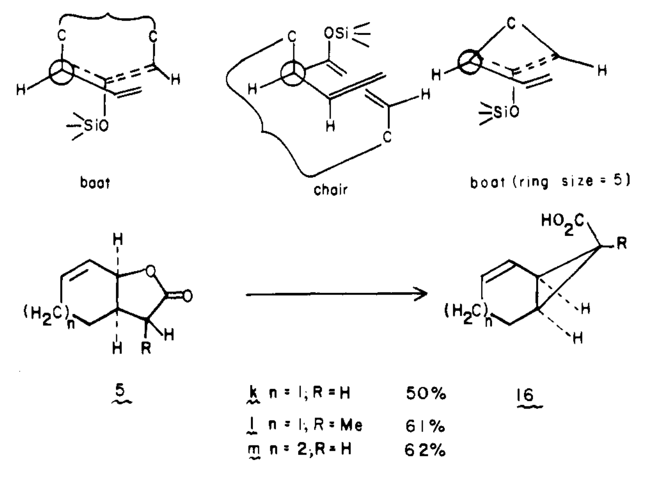
Furthermore, the stereochemical outcome of the **5b** and **5f** entries,[23-25] which were correlated with known compounds, is indicative of a boatlike geometry in the transition state. This topology, which also apparently[26] governs entries **5d**, **e**, **g**, and **h** was already indicated for the Büchi reaction.[3]

The preference is readily understood in terms of the Newman projection figures shown below. The requirement of cis double bonds in both **6** and **7** is such that the chair form would necessitate joining trans-oriented methylene groups through a zero (for the six-membered ring) or one (for the seven-membered ring) carbon bridge. This is clearly impossible in a concerted setting. The boat variation, while far from strain free, involves no such burden. *It will be noted that even a boat topology, in the case of a five-membered version of system* **6**, *would entail an additional increment of strain.*

Three substrates bearing on this question were investigated. The thermolyses of compounds **5k–m** were conducted from 155–175 °C. *After hydrolysis in the usual way, compounds* **16k–m** *were isolated, apparently arising from [1,3] rearrangement.*

The intercession of a [1,3] mutant of the Claisen rearrangement, where the typical [3,3] process is of unusually high energy, is precedented from the work of Arnold.[27] A palladium-mediated variation of this process was recently described by Trost.[28] What is particularly noteworthy about the cases shown here is the virtually complete specificity in favor of the syn isomer. The origin of this effect is not understood at present. See Scheme III.

Scheme III



The ease of obtaining systems of the type **5**, the relatively mild conditions required for their rearrangement, and the access thereby provided to the thermodynamically less stable cis (**8** from the [3,3] process) or syn (**16** from the [1,3] process) isomers render this retrocyclic Claisen reaction of considerable interest. It is our intention to explore in greater detail the mechanistic and stereochemical details of such rearrangements.

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[22] Half-lives for these cases were generally between 0.5 and 2 h. The ketene acetal of compound **5f** was the fastest reacting substrate with a half-life of 35 min at 95 °C.

[23] The product **8b** was previously known.[24] Compound **8f** was correlated with the previously known[25] methyl ester ethylene thioketal of *cis*-2-phenyl-5-oxocyclohexenecarboxylic acid.

[24] (a) Alder, K.; Vogt, W. *Justus Liebigs Ann. Chem.* **1949**, *564*, 120. (b) Rudenko, A. A.; Metlyaeva, S. Y.; Kucherov, V. F. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1970**, 1224.

[25] Ziegler, F. E.; Condon, M. E. *J. Org. Chem.* **1971**, *36*, 3707.

[26] The stereochemistry of these homogeneous acids was not rigorously determined, but the assignment for the moment rests entirely on analogy with cases **5b** and **5f**.

[27] Arnold, R. T.; Kulenović, S. T. *J. Org. Chem.* **1980**, *45*, 891.

[28] Trost, B. M.; Runge, T. A.; Jungheim, L. N. *J. Am. Chem. Soc.* **1980**, *102*, 2840.

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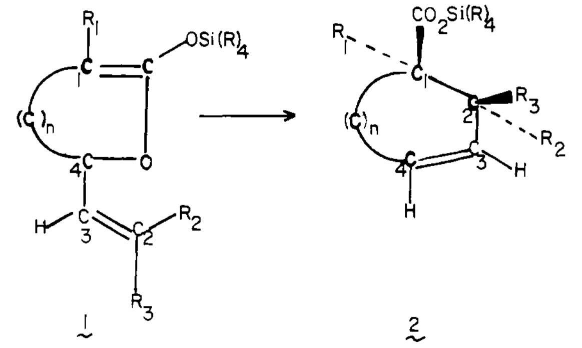
Control of Remote Relative Chiralities: A Stereospecific Total Synthesis of *dl*-Widdrol

Sir:

In the preceding paper,[1] we described the cyclomutative variation of Ireland's allylic ester (silyl) enolate rearrangement.[2] On the basis of the expected[3] boatlike topology of the transition state, the relationship of the geometry of the double bond to the diastereomerism of the sp^3 carbons 1 and 2 is summarized in the expression **1** → **2**.



Below, we consider another stereochemical implication of the process. We sought to demonstrate, by experiment, the relationship of the relative chiralities at C_4 and C_i of the starting lactone derivative, now shown as **3**, with the corresponding chiralities of C_1 and C_i of its rearrangement product, **4**. On reflection, it is recognized that the consequence of this chirality transfer is such that if the vinyl group is, for instance, trans to R in **3** the carbosilyloxy group shall emerge cis to R_1 in **4**. *It should be emphasized that this connectivity involves no suppositions regarding the chair- or boatlike contour of the transition state. It depends only on the assumption of suprafaciality in the chirality transfer.*

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(1) Danishefsky, S.; Funk, R.; Kerwin, J. F., Jr. *J. Am. Chem. Soc.* preceding paper in this issue.

(2) Ireland, R. E.; Mueller, R. H.; Willard, A. K. *J. Am. Chem. Soc.* **1976**, *98*, 2868.

(3) Buchi, G.; Powell, J. E. *J. Am. Chem. Soc.* **1970**, *92*, 3126.

0002-7863/80/1502-6891$01.00/0