cantly shorter than the distances of 1.968 and 1.961 Å observed in $\overline{\mathrm{RhI_3(CO)CPhNMeCPhNMe}}$,[5] and $RhCl_3(CHNMe_2)(PEt_3)_2$,[6] respectively. It is also significantly shorter than other Rh(III)-C(alkyl) single bond distances (2.05-2.08 Å)[7-10] even allowing for the change in covalent radius from C(sp^2) to C(sp^3). The shortness of the Rh-C bond may result from increased back-donation from metal d to the p_z orbital on the trigonal carbon atom. It may also result from ligand constraints. Although short, this Rh-C distance is still longer than the Rh(III)-C(carbonyl) distance (1.89 Å) observed in the rhodium carbonyl complex mentioned above.[5]

The carbene carbon atom has the expected high trans influence, resulting in a Rh-Cl bond which is longer than those observed when chlorine is trans to another chlorine ligand[11] (2.34 Å) or to pyridine[7] (2.339 Å). However, it is shorter than the Rh-Cl distance of 2.531 Å observed when a benzyl carbon atom is the trans ligand.[7]

Within the metallocyclic rings there is some delocalization evident as witnessed by the C(2)-O(1) and C(1)-N(1) bonds being longer than the double bond values (compare C(4)-O(2) and C(3)-N(2)). Similarly N(1)-C(2) is shorter than a C-N single bond (1.43 Å). In the ring involving Rh, C(1), S(1), C(3), and S(2) the C(1)-S(1) and C(3)-S(2) bonds are both intermediate between single and double bonds so here again the possibility of delocalization exists.

The ring involving Rh, C(1), N(1), C(2), and O(1) is essentially planar with only C(2) being displaced by 0.015 Å from the mean plane. The Rh-S(2)-C(3)-S(1)-C(1) ring is slightly puckered with C(3) and C(1) deviating from the mean plane by 0.032 and −0.039 Å, respectively. The stability of this complex may arise in part from resonance stabilization resulting from the extended π system on the ligand and on the nearly coplanar phenyl groups.

Analogous reactions involving benzoyl isocyanate in place of benzoyl isothiocyanate yield five-membered metallocyclic structures, as determined in a routine matter spectroscopically. The present results illustrate the striking differences that may be expected between reactions of isocyanates and isothiocyanates with low-valent transition metal systems.

Acknowledgments. This work was supported by the Ministry of Education of Japan and by the U.S. National Science Foundation. M.C. wishes to thank the National Research Council of Canada for a Postdoctoral Fellowship.

Supplementary Material Available. Tables I and II will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for $4.00 for photocopy or $2.50 for microfiche, referring to code number JACS-75-4748.

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Martin Cowie, James A. Ibers*
Department of Chemistry, Northwestern University
Evanston, Illinois 60201

Yoshio Ishii,* Kenji Itoh, Isamu Matsuda, Fujio Ueda
Department of Synthetic Chemistry
Faculty of Engineering, Nagoya University
Chikusa-ku, Nagoya 464, Japan

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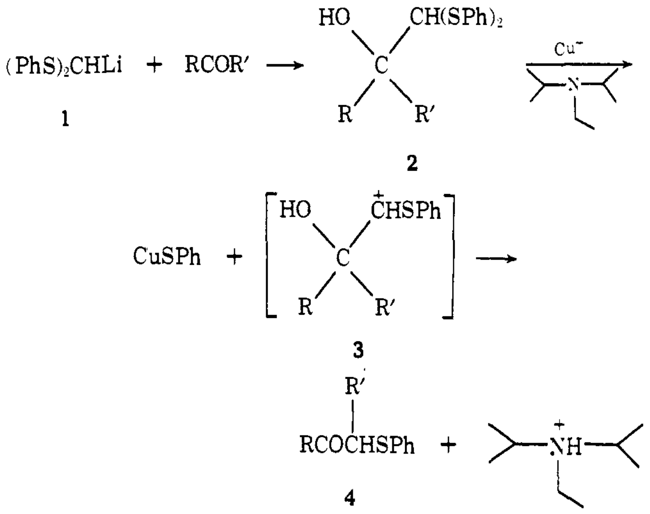
Application of Copper(I)-Induced Thiophenoxide Removal to Ring Expansions or Chain Extensions of Aldehydes and Ketones. Detection, Isolation, and Independent Preparation of the α-Epoxy Thioether Intermediate

Sir:

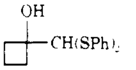
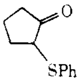
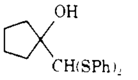
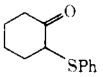
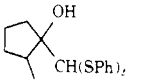
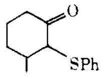
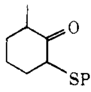
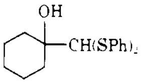
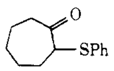
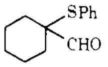
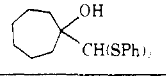
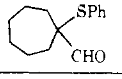
Recent work from this laboratory[1] has demonstrated that sulfur-stabilized carbonium ions can be readily generated in organic solvents under mild conditions by removal of a thiophenoxide ion from a thioacetal or thioketal using soluble cuprous trifluoromethanesulfonate (triflate).[2] The procedure was applied to the syntheses of a variety of vinyl sulfides and of a furan. We now report applications which result in new synthetic procedures and which illustrate the high selectivity of the process.

The α-hydroxydiphenylthioacetals (**2**, 3 mmol in a typical run), readily obtained by the addition of the lithio derivative (**1**) of dithiophenoxymethane to aldehydes and ketones,[3] react with cuprous triflate (6 mequiv) in benzene (15 ml) containing diisopropylethylamine (4 mmol) to give, in most cases, good yields of rearrangement products, **4**, presumably via the intermediate cation **3**.[4]



The procedure provides a method for producing the homologous α-thiophenoxy ketones and it results in ring expansion in the case of cyclic ketones (Table I). The ketonic products thus functionalized are exceedingly useful synthetic intermediates[5] and some would be difficult to prepare by available procedures. This overall insertion process should thus find use in synthesis. Although a number of ring-expansion procedures for ketones are available, none of them lead directly to 2-sulfenylated ketones and most suffer by comparison with the present method with regard to ease of operation and yield.[6,7]

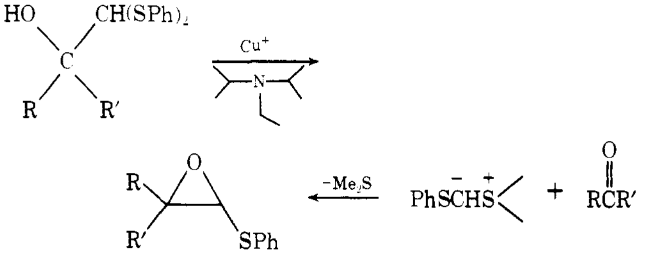
Table I. Yields and Conditions for Rearrangement Reactions

Substrate (% yield from 1)[a,b]	Temp, °C (time, hr)	Product (% yield)[a]
$EtCH(OH)CH(SPh)_2$ (80)	78 (1)	$EtCOCH_2SPh$ (66)
$Et_2C(OH)CH(SPh)_2$ (90)	78 (1)	EtCOCH(SPh)Et (88)
MeC(OH)(*i*-Pr)$CH(SPh)_2$ (85)	78 (1.5)	MeCOCH(SPh)-*i*-Pr (81)
 (86)	46 (2.3)	 (72)
 (81)	78 (1)	 (83)
 (84)[c]	78 (1.5)	 (74),[d]  (9)[d]
 (74)	45[e] (1.5),[f] 56[e] (3)[g]	 (58)  (13)
 (86)	45 (9),[h] 62 (5)[g]	 (78)

[a] Yield of purified material, except where noted. [b] Yields of adducts not optimized. [c] Two stereoisomers (65 and 19%); the major one used for the rearrangement. [d] Yields determined by reduction (Li, NH_3) of the mixture of isomers to 2- and 3-methylcyclohexanone and GLC analysis. [e] When the reaction was performed for 1.3 hr in refluxing toluene, 16% of the ketone and 43% of the aldehyde were produced. [f] Temperature and time for conversion to an unisolated intermediate believed to be the epoxide. [g] Temperature and time for rearrangement of the intermediate to products. [h] For complete conversion to epoxide.

The results in Table I[8] indicate that hydrogen migrates faster than alkyl and that the most highly substituted alkyl group migrates preferentially. The ring expansion proceeds smoothly with the adducts of four-, five-, and six-membered ketones. However, in the latter case, when the temperature is allowed to rise much above 56°, the yield of a minor product, 1-thiophenoxycyclohexanecarboxaldehyde, increases at the expense of the cycloheptanone; in refluxing toluene this aldehyde becomes the major product. The attempted ring expansion of cycloheptanone fails completely; instead 1-thiophenoxycycloheptanecarboxaldehyde (**5**, Table I) is produced in 78% yield.

Careful monitoring of most of the reactions of Table I by thin layer chromatography revealed a reaction intermediate which moves more rapidly than either reactant or product.[9] In the case of the adducts of cyclohexanone and cycloheptanone, solutions rich in the intermediates were obtained by performing the reaction at a lower temperature (~45°) than used for preparation of the rearrangement products (78°). Raising the temperature (Table I) then caused conversion to the rearrangement products. Nearly pure (by ^{1}H NMR) samples of the intermediates were obtained in the cases of the adducts from diethyl ketone and cycloheptanone by performing the reaction at 45° and passing the product rapidly through a short silica column to remove copper salts and amine. Spectra (ir and ^{1}H NMR) of these materials and a less pure substance obtained in the same way from the adduct of cyclohexanone are consistent with structures of α-epoxy thioethers (**6**). These compounds, and analogous ones prepared by another procedure (see below), are unstable to the usual methods of purification but an analytical sample of that (**6**; R,R′ = $-(CH_2)_6-$) from cycloheptanone was prepared by preparative TLC on the slightly basic E. Merck aluminum oxide G (type E):[10] ^{1}H NMR spectrum δ 1.4-2.13 (m, 12 H), 4.10 (s, 1 H), 7.08-7.55 (m, 5 H); the mass spectrum was almost identical with that of 1-thiophenoxycycloheptanecarboxaldehyde (**5**), 234 (62), 205 (100).



6 **7**

Treatment of cycloheptanone (3.6 mmol) with the ylide **7**[11] (prepared at −20° from 3.7 mmol of the sulfonium bromide[11] and 3.8 mmol of *n*-butyllithium in 35 ml of THF) at −20° and then room temperature yielded the same (TLC, NMR) epoxide (66%) contaminated with 6% of *cis*- and *trans*-1,2-dithiophenoxyethene.[11] Similarly contaminated epoxythioethers could be prepared from diethyl ketone (product identical by NMR with that prepared as above), propionaldehyde (two stereoisomers), and cyclopentanone.

The only previous report of an α-epoxythioether is that of Tavares and Estep[12] who found that benzaldehyde and pivalaldehyde (but not ketones) react with chloromethyl *p*-tolyl sulfide in the presence of potassium *tert*-butoxide to give the *p*-tolyl analogs of **6** (R = phenyl or *tert*-butyl, R′ = H).[13] The two methods of preparation of these interesting compounds reported here are quite convenient and apparently general and we should like to encourage a study of their chemical properties by others.[13]

It is significant that under our reaction conditions carbonium ions can be produced by attack of copper(I) on sulfur even in the presence of acid-sensitive tertiary alcohol functions. However, it is much more striking that, at a given temperature, production of a carbonium ion from a thioacetal is considerably faster than generation of the same type of (and possibly identical) carbonium ion from the extremely acid sensitive α-epoxy thioether; this follows from the fact that the latter forms in high yield from a thioacetal and a cuprous ion. This great selectivity of the soft acid copper(I) toward sulfur suggests that our procedure should find use in the production of carbonium ions by thiophenoxide removal even in the presence of functional groups which are capable of rapid reaction with (hard) protonic acids to form carbonium ions of a different type.[15]

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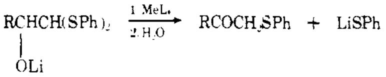
(4) A somewhat related transformation has been reported wherein the adduct of **1** with an aldehyde, upon treatment with MeLi, undergoes an apparent carbenoid rearrangement:



$$\underset{\displaystyle \mathrm{OLi}}{\mathrm{RCHCH(SPh)_2}} \xrightarrow[2.\ \mathrm{H_2O}]{1.\ \mathrm{MeLi}} \mathrm{RCOCH_2SPh} + \mathrm{LiSPh}$$

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(8) Satisfactory elemental and spectroscopic analyses have been obtained for all new compounds.

(9) No intermediate was detectable from the adduct of cyclobutanone.

(10) Attempts to purify the other epoxides mentioned here by this method were not made.

(11) Y. Hayasi, M. Takaku, and H. Nozaki, *Tetrahedron Lett.*, 3179 (1969).

(12) D. F. Tavares and R. E. Estep, *Tetrahedron Lett.*, 1229 (1973).

(13) These authors reported that one of the epoxy thioethers from benzaldehyde rearranged in the presence of BF_3 etherate to α-*p*-tolylthiophenylacetaldehyde by apparent migration of the sulfur bearing group. This may be analogous to the rearrangement **6** (R,R′ = $-(CH_2)_6-$) $\rightarrow$ **5** observed when the former, produced in situ, is heated to 62° (Table I). It is of interest that the other epoxy thioethers under our conditions rearrange with carbon (or hydrogen) migration. We have also observed that **6** (R,R′ = $-(CH_2)_6-$) rearranges to **5** rapidly at room temperature in the presence of catalytic quantities of BF_3 etherate or of CF_3CO_2H or slowly (>30 hr) when heated at reflux in benzene containing cuprous triflate and amine. Surprisingly, however, the epoxide was recovered unchanged after treatment with LiBr–HMPA in refluxing benzene, conditions which isomerize other epoxides.[14]

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Theodore Cohen,* David Kuhn, J. R. Falck
Department of Chemistry, University of Pittsburgh
Pittsburgh, Pennsylvania 15260

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Interpretation of Fluorescence Detected Circular Dichroism Data

Sir:

Recently Turner et al.[1] reported on the use of fluorescence for detecting circular dichroism (CD) in molecular systems. We have also been investigating this technique and wish to report on some similarities and differences between their results and ours. In particular the approach taken by us on the analysis of results provides some guidance on how the contributions of various competing mechanisms might be disentangled.

It is known that circular dichroism is a powerful technique for investigating molecular structure. Until recently all such investigations were carried out in transmission. More recently Schlessinger and Steinberg[2,3] have shown that measurement of the circular polarization of the light emitted in fluorescence can often provide the same type of information. In the event that there is molecular rearrangement or energy transfer while the molecule is in the excited state, the Schlessinger and Steinberg technique can provide information otherwise not obtainable through other means. In another development Pao[4] and Einhorn et al.[5] have shown that CD may also be measured in reflection. However the reflection method suffers from some practical limitations, the need for extreme accuracy in optical alignment being one of these.

The transmission experiment is perfectly satisfactory except when the samples of interest become nearly opaque and/or when nonhomogeneous samples (such as cellular structure of nonuniform composition) are involved. Under such circumstances the technique reported by Turner et al. and studied by us constitutes a powerful alternate approach. Another circumstance of interest is the one emphasized by Turner et al., namely, the possibility of disentangling two overlapping CD species, only one of which is fluorescent.

However, use of the fluorescence technique brings with it certain complexities in the interpretation of results. Some of these are mentioned in the Turner et al. communication and we wish to expand on these in this note.

Laser excitation by an Argon ion laser at three discrete wavelengths, namely, 458, 476, and 488 nm, were used in our experiment. An Isomet Model 401-A Pockel cell is used to modulate the polarization of the incident beam. The fluorescence output is detected either in the forward direction and/or at 90° to the excitation beam. The light output is detected with a Hamatsu Type R375 photomultiplier, and the resulting electrical signal is processed through a P.A.R. Model HR-8 lock-in amplifier. The DC output voltage of the PMT is held constant by automatic control of the photomultiplier high voltage supply. The sensitivity and other CD measurement characteristics of this spectropolarimeter are similar to those of commercially available instruments, *provided laser excitation is used.*

The system studied by us is the polysaccharide chondroitin sulfate Type A (CSA) complexed with acridine orange dye. The system turned out to be a very difficult system. As we proceeded, we found that results varied appreciably depending on the ratio of the concentrations of CSA and dye and on whether the dye was added to the polymer solution or whether polymer was added to a dye solution. Furthermore CD varied drastically with temperature. After we had unraveled or at least had characterized these trends, we find that the CD detected in fluorescence agreed with that obtained in transmission in general trends but could be off by a scaling factor (0.5–6) which varied from case to case.

In interpretation of data we represented possible systems somewhat differently compared to the scheme used in the Turner publication. We feel that two basic types of situation may be present in the FDCD experiment.

The first and simplest situation arises when an optically active *nonfluorescent* material is present with another fluorescent nonactive material. Near the front surface of the sample where the intensity of the alternately left then right circularly polarized incident beam is constant, the fluorescence output is also constant. However, for an interior point of the sample there are variations in the incident light inten-