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Markownikoff Two-Step Hydrolithiation of α-Olefins. Transformation of Secondary and Tertiary Alkyl Phenyl Sulfides to the Relevant Alkyllithium Reagents

Constantinos G. Screttas* and Maria Micha-Screttas

The National Hellenic Research Foundation, Athens 501/1, Greece

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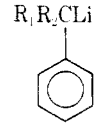
The transformation of a number of α-olefins to the relevant secondary and tertiary alkyllithium reagents has been accomplished in two steps by first converting them to the corresponding alkyl phenyl sulfides through their acid-catalyzed reaction with thiophenol, and second by cleaving the sulfides with lithium in tetrahydrofuran (THF). The overall yields ranged from ~35 to 80%, based on the isolated carboxylic acids after carbonation. Secondary and tertiary benzylic alkyl phenyl sulfides have been synthesized by alternative routes and cleaved by lithium naphthalene to the corresponding benzylic type organolithium reagents. Some of them were converted to other organoalkali reagents; e.g., $Ph_2C(CH_3)M$ (M = Li, Na, K), $LiCH(Ph)(CH_2)_nCH(Ph)Li$ (n = 3,4,5,6,10), $LiOC(Ph)(R)CH(Ph)Li$ (R = CH_3, Ph), and $LiOCH_2CH_2CH(Ph)Li$. The latter two examples represent cases of dianions formally equivalent to those derived from two-electron reductive opening of oxirane and oxetane rings, respectively. The lithiooxy sulfide $PhCH(OLi)CH(Ph)SPh$ underwent a facile C–S as well as C–O bond fission by lithium naphthalene and was transformed to stilbene dianion $(PhCH{=}CHPh)^{2-}$.

The conventional method of preparation of organolithium reagents depends almost exclusively on the availability of the corresponding chlorides and bromides.[1] Metalation by simple organolithium and organosodium compounds is an alternative method for preparing metal derivatives of aromatic compounds.[2] The synthesis of metal derivatives such as 1 by these two methods may present some difficulties. The metalation method is limited by the lack of regiospecificity because it usually gives rise to complex mixtures of side chain as well as ring metalated products, and the conventional method is seldom usable due to Wurtz coupling reaction.



1, R = Li, Na, K

One of the most reliable methods for preparing organoalkali reagents of unambiguous structure is the metalative cleavage reaction shown in eq 1.[3] However, ethers of this type are not as readily available as thioethers.

$$PhC(CH_3)_2OCH_3 \xrightarrow{Na-K} PhC(CH_3)_2K + CH_3OK \quad (1)$$

Recently, we reported[4] the transformation of α-olefins to the corresponding primary alkyllithium reagents by the two-step sequence shown in eq 2. Here we wish to describe the preparation of secondary and tertiary organolithiums by means of the process of eq 3.

$$R_1R_2C{=}CH_2 + PhSH \xrightarrow{R\cdot} R_1R_2CHCH_2SPh \xrightarrow[THF]{Li} R_1R_2CHCH_2Li + PhSLi \quad (2)$$

$$R_1R_2C{=}CH_2 + PhSH \xrightarrow{H^+} R_1R_2C(CH_3)SPh \xrightarrow[THF]{Li} R_1R_2C(CH_3)Li + PhSLi \quad (3)$$

The acid-catalyzed addition of thiophenol to α-olefins is almost as facile as the first step of eq 2. The fundamental difference, of course, lies in the orientation of the addition which gives the Markownikoff adduct.

Besides the fact that sulfides can be more readily accessible through the first reaction of eq 3 than the corresponding ethers, *an additional advantage is offered by the more facile* cleavability of C–S vs. C–O bonds by either alkali metals or aromatic radical anions.[4] Thus, the cleavage step in eq 3 can be run at low temperatures, where the highly reactive secondary and tertiary organolithium reagents can survive without reacting with the THF medium[5] in which they are prepared. It should be pointed out that the steps of eq 3 accomplish the addition of lithium hydride to an olefin in the Markownikoff orientation.

Since secondary and tertiary alkyl phenyl sulfides are available through alternative routes, we have synthesized a number of them and studied their transformation to the corresponding alkyllithium reagents. A small number of them have also been converted to the corresponding organosodium or organopotassium reagents.

Results and Discussion

Perchloric acid (70%), $pK_a = -10$, was used as a catalyst for the addition of thiophenol to α-olefins. The secondary and tertiary alkyl phenyl sulfides thus formed were isolated in yields ranging from about 65 to 90% (see Table I). Olefins such as 1,1-diphenylethylene and styrenes had to be reacted with thiophenol under an inert atmosphere; otherwise, the product was contaminated with the anti-Markownikoff adduct which could not be separated by distillation. Olefins, which on protonation give a tertiary carbenium ion, react exothermically with thiophenol in the presence of 70% perchloric acid.[6] In contrast, olefins of the type $RCH{=}CH_2$ appear to be less reactive than the previously mentioned ones. In the latter case, higher reaction temperatures and longer reaction times had to be employed in order to obtain secondary alkyl phenyl sulfides in satisfactory yields.

The cleavage of secondary and tertiary alkyl phenyl sulfides

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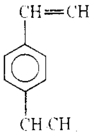
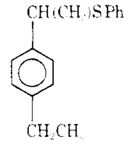
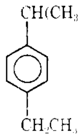
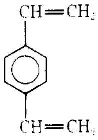
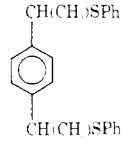
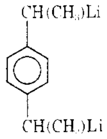
Table I. Markownikoff Hydrolithiation of α-Olefins in Two Steps

olefin	registry no.	sulfide (% yield)	registry no.	alkyllithium	registry no.	% yield[a] by	
						$Li^+/Naph^{-\cdot}$	Li disp.[g]
$CH_3(CH_2)_4CH{=}CH_2$	592-76-7	$CH_3(CH_2)_4CH(CH_3)SPh$ (70)	13921-14-7	$CH_3(CH_2)_4CH(CH_3)Li$	68602-04-0		78 ca.
$CH_3(CH_2)_5CH{=}CH_2$	111-66-0	$CH_3(CH_2)_5CH(CH_3)SPh$ (80)	13921-16-6	$CH_3(CH_2)_5CH(CH_3)Li$	61182-93-2		72 ca.
$CH_3(CH_2)_3C(Et){=}CH_2$	1632-16-2	$CH_3(CH_2)_3C(Et)(CH_3)SPh$ (85)	68602-00-6	$CH_3(CH_2)_3C(Et)(CH_3)Li$	61182-94-3		54 ca.
$(CH_3)_3CCH{=}CH_2$	558-37-2	$(CH_3)_3CCH(CH_3)SPh$	54495-70-4	$(CH_3)_3CCH(CH_3)Li$	68602-05-1		50 ca.
t-$BuCH_2C(CH_3)_2CH_2C(CH_3){=}CH_2$	14031-86-8	t-BuSPh (39) + t-$BuCH_2C(CH_3)_2SPh$ (13)	3019-19-0 68602-01-7	t-BuLi t-$BuCH_2C(CH_3)_2Li$	594-19-4 68602-06-2	49[b]	78 uc. 39 uc.
cyclohexene	110-83-8	c-$C_6H_{11}SPh$ (85)[c]	7570-92-5	c-$C_6H_{11}Li$	10074-42-7	100	
$PhCH{=}CH_2$	100-42-5	$PhCH(CH_3)SPh$ (68)	21213-26-3	$PhCH(CH_3)Li$	13950-05-5	54	
$PhC(CH_3){=}CH_2$	98-83-9	$PhC(CH_3)_2SPh$ (63)	4148-93-0	$PhC(CH_3)_2Li$	27271-53-0	80	
$Ph_2C{=}CH_2$	530-48-3	$Ph_2C(CH_3)SPh$ (88)	60731-09-1	$Ph_2C(CH_3)Li$	67997-44-8	82	93 uc.
	3454-07-7	 (76)	68602-02-8		68602-07-3	75[d]	
	105-06-6	 (80)	68602-03-9		68602-08-4	d	
e		sec-BuSPh	14905-79-4	sec-BuLi	598-30-1		60 uc.
f		t-AmSPh	41469-79-8	t-AmLi	68602-09-5		79 uc.

[a] Taken synonymous to the yield of carboxylic acid after carbonation. All known acids had correct NMR spectra. [b] Plus 48% yield of t-$BuC_{10}H_8Li$. [c] Prepared by photochemically catalyzed addition of thiophenol to cyclohexene. [d] It is not a clean reaction. [e] Prepared from *sec*-butyl bromide and thiophenol in aqueous NaOH. [f] Prepared from *tert*-amyl chloride and thiophenol.[11] [g] ca. = in the presence of a catalytic amount (8%) of naphthalene; uc. = uncatalyzed.

by lithium naphthalene appears to be a complicated reaction. Besides the expected alkyllithium compound, carbanions which are derivatives of alkyldihydronaphthalene are also present in the reaction products. In this respect, sulfides appear to behave in a parallel manner to their halogen counterparts.[7,8] For example, *tert*-butyl phenyl sulfide and lithium naphthalene at about −50 °C gave an almost equimolar mixture of *tert*-butyllithium and t-$BuC_{10}H_8^-Li^+$. The only secondary sulfide which gave cleanly the desired alkyllithium reagent was the alicyclic one, c-$C_6H_{11}SPh$. Even in this case the analogy between sulfides and halides still holds; cyclohexyl chloride gives good yields of cyclohexyllithium with lithium naphthalene in THF.[9]

In order to avoid the undesirable reaction which leads to the formation of $RC_{10}H_8^-Li^+$, the cleavage reaction was attempted with lithium dispersion in THF. By this method yields of 50–80% of alkyllithium reagents were realized in 2.5–3.0 h at temperatures around −40 °C or lower (see Table I). Solutions of alkyllithium compounds thus prepared exhibited a yellowish color.[10] It should be noted that organolithium products were characterized and their yields determined on the basis of the isolated carboxylic acids after carbonation.

In the remainder of this section we will limit our discussion of the cleavage reaction to the sulfides prepared from styrenes and 1,1-diphenylethylene, and refer also to the synthesis and metalative cleavage of benzylic sulfides prepared by alternative routes.[11,12]

We found that benzhydryl phenyl sulfide, Ph_2CHSPh, can be metalated in high yields with butyllithium and THF as the catalyzing Lewis base. The resulting reagent in eq 4 is identical with the one derived from the "thiophilic" addition of phenyllithium to thiobenzophenone[13] (eq 5). Reagent $Ph_2C(Li)SPh$ reacts just like $PhCH(Li)SPh$[12] with primary and secondary alkyl bromides and affords the corresponding alkylated sulfides in very good yields (see Table II).

$$Ph_2CHSPh \xrightarrow[THF]{BuLi} Ph_2C(Li)SPh \xrightarrow{RBr} Ph_2C(R)SPh, \xrightarrow{Li^+C_{10}H_8^{-\cdot}} Ph_2C(R)Li \quad (4)$$

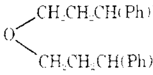
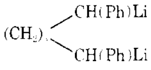
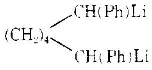
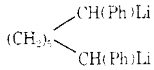
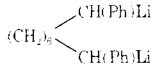
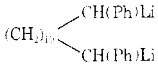
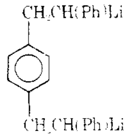
$$Ph_2C{=}S + PhLi \rightarrow Ph_2C(Li)SPh \quad (5)$$

Tertiary benzylic sulfides react very cleanly with lithium naphthalene and give the desired lithium reagents in very good yields. Of the secondary benzylic sulfides, PhCH(R)SPh, satisfactory results were obtained only with R $\neq$ CH_3. Phenylethyl phenyl sulfides with ring substituents (alkyl or methoxy) in the benzylic moiety on cleavage with lithium naphthalene gave complex mixtures of ArCH(Li)R and $ArCH(R)C_{10}H_8^-Li^+$[14] (see Table II).

1- and 2-naphthylethyl phenyl sulfides, $C_{10}H_7CH(CH_3)SPh$, do not cleave by either lithium naphthalene or lithium dispersion. Obviously, the great electron affinity of the naphthyl group makes the sulfide radical anion particularly stable with respect to fission.[15]

Concerning the cleavage of the sulfides prepared via the reaction sequence of eq 4, it should be pointed out that this method gives access to $Ph_2C(R)Li$ [for R = n-alkyl ($\neq$ CH_3)] by an alternative route to the one of $Ph_2C{=}CH_2$ + R′Li.[16] Furthermore, it appears that in the case of R = secondary alkyl, the only convenient synthesis of $Ph_2C(R)Li$ is via the

Table II. Transformation of Certain Benzylic Type Phenyl Sulfides to Alkyllithium Reagents

starting materials	registry no.	sulfide (% yield)	registry no.	alkyllithium	registry no.	% yield by	
						$Li^+ Naph^{-}\cdot$	Li disp.
Ph_2CHOH, PhSH[a]	91-01-0, 108-98-5	Ph_2CHSPh (86)		Ph_2CHLi	881-42-5	91	90
Ph_3COH, PhSH	76-84-6	Ph_3CSPh (93)	16928-73-7	Ph_3CLi	733-90-4	95	92
$PhCH(CH_3)OH$, PhSH	98-85-1	$PhCH(CH_3)SPh$	21213-26-3	$PhCH(CH_3)Li$		54	0
m-$CH_3C_6H_4CH(CH_3)OH$, PhSH	7287-81-2	m-$CH_3C_6H_4CH(CH_3)SPh$ (63)	68602-10-8	m-$CH_3C_6H_4CH(CH_3)Li$	68602-19-7		[b]
p-$CH_3OC_6H_4CH(CH_3)OH$, PhSH	3319-15-1	p-$CH_3OC_6H_4CH(CH_3)SPh$ (72)	60702-13-8	p-$CH_3OC_6H_4CH(CH_3)Li$	68602-20-0		[b]
$PhCH(t\text{-}Bu)OH$, PhSH	3835-64-1	$PhCH(t\text{-}Bu)SPh$ (70)	68602-11-9	$PhCH(t\text{-}Bu)Li$	68602-21-1	100	
1-$C_{10}H_7CH(CH_3)OH$, PhSH	1517-72-2	1-$C_{10}H_7CH(CH_3)SPh$ (80)	68602-12-0	1-$C_{10}H_7CH(CH_3)Li$	68602-22-2	0	0
2-$C_{10}H_7CH(CH_3)OH$, PhSH	7228-47-9	2-$C_{10}H_7CH(CH_3)SPh$ (100)	68602-13-1	2-$C_{10}H_7CH(CH_3)Li$	68602-23-3	0	0
$PhCH_2SPh$, n-BuBr[c]	831-91-4, 109-65-9	$PhCH(n\text{-}Bu)SPh$ (77)	68602-14-2	$PhCH(n\text{-}Bu)Li$	68602-24-4	78	
$PhCH_2SPh$, sec-BuBr	78-76-2	$PhCH(sec\text{-}Bu)SPh$ (78)	68602-15-3	$PhCH(sec\text{-}Bu)Li$	68602-25-5	97	
$PhCH_2SPh$, $PhCH_2Cl$	100-44-7	$PhCH(CH_2Ph)SPh$ (92)	31616-44-1	$PhCH(CH_2Ph)Li$	68602-26-6	79	
$CH_2(SPh)_2$, n-BuBr	3561-67-9	n-$BuCH(SPh)_2$ (78)	56651-44-6	n-$Bu(SPh)CHLi$	68602-27-7	90	78
Ph_2CHSPh, n-BuBr	21122-20-3	$Ph_2C(n\text{-}Bu)SPh$ (100)	68602-16-4	$Ph_2(n\text{-}Bu)Li$	68602-28-8	72	
Ph_2CHSPh, sec-BuBr		$Ph_2C(sec\text{-}Bu)SPh$ (100)	68602-17-5	$Ph_2C(sec\text{-}Bu)Li$	68602-29-9	92	
[d]		$Ph_2CHOCH_2CH_2CH(Ph)SPh$ (100)	68602-18-6	$LiOCH_2CH_2CH(Ph)Li$	68602-30-2	98	
$PhCH_2SPh$, $O(CH_2CH_2Cl)_2$	111-44-4	$O(CH_2CH_2CH(Ph)SPh)_2$ (92)	68602-31-3	 $O\begin{cases}CH_2CH_2CH(Ph)Li\\CH_2CH_2CH(Ph)Li\end{cases}$	68602-38-0	100	
$PhCH_2SPh$, $Br(CH_2)_3Br$	109-64-8	$(CH_2)_3(CH(Ph)SPh)_2$ (84)	68602-32-4	 $(CH_2)_3\begin{cases}CH(Ph)Li\\CH(Ph)Li\end{cases}$	68602-39-1	91	
$PhCH_2SPh$, $Br(CH_2)_4Br$	110-52-1	$(CH_2)_4(CH(Ph)SPh)_2$ (89)	68602-33-5	 $(CH_2)_4\begin{cases}CH(Ph)Li\\CH(Ph)Li\end{cases}$	68602-40-4	100	68
$PhCH_2SPh$, $Br(CH_2)_5Br$	111-24-0	$(CH_2)_5(CH(Ph)SPh)_2$ (86)	68602-34-6	 $(CH_2)_5\begin{cases}CH(Ph)Li\\CH(Ph)Li\end{cases}$	68602-41-5	95	
$PhCH_2SPh$, $Br(CH_2)_6Br$	629-03-8	$(CH_2)_6(CH(Ph)SPh)_2$ (91)	68602-35-7	 $(CH_2)_6\begin{cases}CH(Ph)Li\\CH(Ph)Li\end{cases}$	68602-42-6	96	
$PhCH_2SPh$, $Br(CH_2)_{10}Br$	4101-68-2	$(CH_2)_{10}(CH(Ph)SPh)_2$	68602-36-8	 $(CH_2)_{10}\begin{cases}CH(Ph)Li\\CH(Ph)Li\end{cases}$	68602-43-7	72	
$PhCH_2SPh$, p-$C_6H_4(CH_2Br)_2$	623-24-5	p-$C_6H_4(CH_2CH(Ph)SPh)_2$	68602-37-9		68602-44-8	75	
$PhCH_2SPh$, $PhCH{=}O$	100-52-7	$PhCH(OH)CH(Ph)SPh$ (83)	54130-67-5	$(PhCH{=}CHPh)^{2-}Li_2^{2+}$	13555-77-6	41[e] (84[f])	
$PhCH_2SPh$, $Ph(CH_3)C{=}O$	98-86-2	$PhC(OH)(CH_3)CH(Ph)SPh$ (74)	54486-19-0	$PhC(OLi)(CH_3)CH(Ph)Li$	68602-45-9	55	
$PhCH_2SPh$, $Ph_2C{=}O$	119-61-9	$Ph_2C(OH)CH(Ph)SPh$ (86)	54130-68-6	$Ph_2C(OLi)CH(Ph)Li$	68602-46-0	66	

[a] See ref 11 for the transformation of arylcarbinols to sulfides. [b] It is not a clean reaction. [c] See ref 12. [d] The synthesis of this ether sulfide will be described in a separate publication. [e] With 2 equiv of Li^+ $Naph^{-}\cdot$. [f] With 4 equiv of Li^+ $Naph^{-}\cdot$.

sulfide route because the carbanion $Ph_2C(R_1R_2CH)^-$ cannot be prepared either from diphenylethylene or from the corresponding carbon acid by metalation.

The cleavage of the sulfide $Ph_2C(CH_3)SPh$ by Li, Na, and K metals has been studied in more detail (see Tables I and III). (1,1-Diphenylethyl)lithium, -sodium, and -potassium have been prepared from this sulfide in very good yields. All three metal derivatives appear to be stable in THF solution (suspension), and their preparation can be run at room temperature. The solubility in THF of the derivatives is Li > K ≫ Na. Cleavage of the sulfide with metal chips in THF is possible with lithium and potassium, but not with sodium. A good yield of $Ph_2C(CH_3)Na$ was realized only by employing a sodium dispersion.

Table III also summarizes the results from the cleavage of certain benzylic sulfides with sodium and potassium. Worthy of note could be the dramatic catalytic effect of naphthalene in the cleavage of trityl phenyl sulfide. In the absence of

Table III. Some Alkylsodium and Alkylpotassium Reagents Prepared from Sulfides

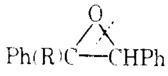
sulfide (mmol)	metal (g)	$C_{10}H_8$, g	THF, mL	Et_2O, mL	rxn temp, C	rxn time, h	% yield	registry no.
$PhC(CH_3)_2SPh$ (100)	K (8.1)	26	150	150	−60 to −45	1	80	3003-91-6
$Ph_2C(CH_3)SPh$ (86)	K (7.0)	22	150	150	−65 to −50	1	76	68602-47-1
$Ph_2C(CH_3)SPh$ (20)	Na (1.0)[a]	0	50	0	RT	5.25	5	68602-48-2
$Ph_2C(CH_3)SPh$ (20)	K (1.65)[a]	0	50	0	RT	2.25	71	
$Ph_2C(CH_3)SPh$ (20)	Na (1.3)[b]	0	50	0	RT	2	89	
$PhC(CH_3)_2SPh$ (20)	K (1.6)[b]	0	50	0	−20 to −10	1	88	
$(CH_2)_3(CH(Ph)SPh)_2$ (5)	K (0.8)	2.9	30	0	−70 to −55	0.25	100	68602-49-3
$(CH_2)_6(CH(Ph)SPh)_2$ (5)	K (0.8)	3.0	35	40	−55 to −30	1.5	98	68602-50-6
$(CH_2)_4(CH(Ph)SPh)_2$ (10)	K (1.6)	5.5	120	80	−50 to −25	0.3	100	68602-51-7
Ph_3CSPh (5)	Na (0.23)[a]	0	25	0	RT	24	0	
Ph_3CSPh (5)	Na (0.23)[a]	0.3	25	0	RT	24	90	4303-71-3
Ph_3CSPh (5)	K (0.4)	0	25	0	RT	24	[c]	
Ph_3CSPh (5)	K (0.4)	0.3	25	0	RT	24	88	1528-27-4
Ph_2CHSPh (10)	K (0.8)[a]	0	25	0	RT	24	[c]	
Ph_2CHSPh (10)	Na (0.46)	0.3	25	0	RT	24	75	5152-68-1

[a] Metal chips. [b] Metal dispersion. [c] It is not a clean reaction.

naphthalene, sodium metal chips in 24 h failed to produce any red color in the solution of Ph_3CSPh in THF at room temperature, whereas in the presence of 20 mol % naphthalene an almost quantitative yield of Ph_3CNa was obtained. The uncatalyzed reaction of Ph_3CSPh with potassium metal is not a clean reaction.

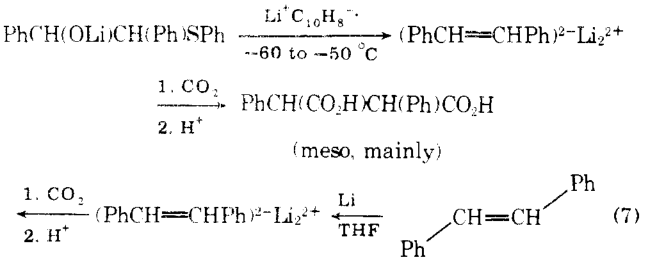
The disulfides $PhSCH(Ph)(CH_2)_nCH(Ph)SPh$ are cleaved by either lithium or potassium naphthalene to the corresponding dilithio or dipotassio derivatives rather cleanly. This is in contrast to the behavior of the sulfides $PhS(CH_2)_nSPh$, which have been shown to react with lithium naphthalene in a complicated manner.[4] These benzylic dicarbanions appear to be unstable in THF at room temperature.

The lithiooxy sulfides, Ph(R)C(OLi)CH(Ph)SPh (R = Ph, CH_3), on cleavage with lithium naphthalene afforded the expected oxocarbodianions in 66 and 55% yields, respectively. These dianions could be thought of as equivalent to those derived by two-electron reductive cleavage of the oxirane **2** (eq 6). For R = H, the reaction took a somewhat unexpected course. Instead of the oxocarbodianion, PhCH(OLi)-CH(Ph)Li, stilbene dianion formed (eq 7). This rather facile reductive fission of a lithiooxy group by an aromatic radical anion does not appear to be as common as is in the reduction of benzylic alcohols by sodium in liquid ammonia.[17] Perhaps, the observed unique behavior of this hydroxy sulfide could be accounted for on considering the marked gain in thermochemical stability of the system, which is caused by the expansion of the original π-conjugate system from one with two noninteracting sets of six π orbitals to another with 14 conjugate π orbitals, and this without any skeletal reorganization.



2

$$\mathrm{Ph(R)C(OH)CH(Ph)SPh} \xrightarrow[\text{2. } Li^+C_{10}H_8^{-\cdot}]{\text{1. BuLi}} \mathrm{Ph(R)C(O^-)(Ph)CH^-}\ (= 2e^- + \mathbf{2}) \quad (6)$$



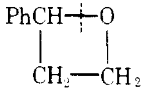
$$\mathrm{PhCH(OLi)CH(Ph)SPh} \xrightarrow[-60\text{ to }-50\ ^\circ C]{Li^+C_{10}H_8^{-\cdot}} \mathrm{(PhCH{=}CHPh)^{2-}Li_2^{2+}}$$

$$\xrightarrow[\text{2. } H^+]{\text{1. } CO_2} \mathrm{PhCH(CO_2H)CH(Ph)CO_2H}$$

(meso, mainly)

$$\xleftarrow[\text{2. } H^+]{\text{1. } CO_2} \mathrm{(PhCH{=}CHPh)^{2-}Li_2^{2+}} \xleftarrow[\text{THF}]{\text{Li}} \quad (7)$$

The sulfide ether, $PhCH(SPh)CH_2CH_2OCHPh_2$, was cleaved by lithium naphthalene to a mixture of Ph_2CHLi and $PhCH(Li)CH_2CH_2OLi$. The latter oxocarbodianion is formally equivalent to the one resulting from the two-electron reductive opening of the oxetane **3** in a regiospecific manner (eq 8).



3

$$\mathrm{PhCH(SPh)CH_2CH_2OCHPh_2} \xrightarrow[-Ph_2CHLi,\ -PhSLi]{Li^+C_{10}H_8^{-\cdot}} \mathrm{^-OCH_2CH_2(Ph)CH^-}\ (= 2e^- + \mathbf{3}) \quad (8)$$

The *gem*-disulfide, *n*-BuCH(SPh)$_2$, was found to undergo cleavage with either 2 equiv of $Li^+C_{10}H_8^{-\cdot}$ or lithium dispersion in THF and a catalytic amount of naphthalene according to eq 9. The lithio derivative, *n*-BuCH(Li)SPh, is not accessible through metalation with *n*-BuLi and THF, which works quite well for the metalation of thioanisole[18] only.

$$n\text{-}\mathrm{BuCH(SPh)_2} \xrightarrow{2Li^+C_{10}H_8^{-\cdot}} n\text{-}\mathrm{BuCH(Li)SPh}$$

$$\not\leftarrow \mathrm{RLi} + n\text{-}\mathrm{BuCH_2SPh} \quad (9)$$

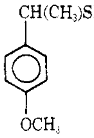
Conclusion

α-Olefins can be converted to alkyllithium reagents of the structures $R(CH_3)CHLi$ and $R_1R_2(CH_3)CLi$ by a two-step sequence involving (1) the conversion of the olefin to the corresponding secondary or tertiary alkyl phenyl sulfide and (2) the cleavage of the sulfide with lithium dispersion in THF. Benzylic type alkyl phenyl sulfides prepared from styrenes or, more conveniently, by alternative routes on cleavage with aromatic radical anions give access to organolithium (or other organoalkali) reagents of the structures $Ph_2C(R)Li$ and $PhCH(R)Li$, in which the R group can be varied rather widely.

Experimental Section

Proton magnetic resonance spectra were recorded with a Varian Associates A-60A NMR spectrometer. Chemical shifts are reported in ppm downfield from Me_4Si as follows: ppm (multiplicity, coupling constant, number of protons, and the segment to which the hydrogens

Table V. Boiling or Melting Points of the Known Alkyl Phenyl Sulfides

sulfide	mp or bp (mm), °C	lit. mp or bp (mm), °C	ref [a]
sec-BuSPh	50–52 (0.05)	63.5 (1.0)	*b*
t-BuSPh	81–82 (6.0)	73 (5.0)	*c*
t-AmSPh	55–56 (0.05)	91–91.3 (6.0)	*c*
$CH_3(CH_2)_5CH(CH_3)SPh$	92 (0.15)	178 (20)	*d*
$PhCH(CH_3)SPh$	113–116 (0.5)	163–164 (15)	*e*
Ph_2CHSPh	74 (MeOH)	78	*f*
Ph_3CSPh	102–104 (MeOH)	106	*f*
$PhCH_2SPh$	40–41 (MeOH)	42	*g*
c-$C_6H_{11}SPh$	73–76 (0.07)	126 (13)	*h*
	120–123 (0.05)	*l*	*i*
$PhCH_2CH(Ph)SPh$	31–32 (MeOH)	170–178 (0.05)	*j*
$CH_2(SPh)_2$	38–39 (hexane)	39.5–40.5	*k*

[a] As a general reference, see, for example, "Organic Chemistry of Divalent Sulfure", Vol. 2, E. E. Reid, Ed., Chemical Publishing Co., New York, 1960. [b] A. C. Cope, D. E. Morrison, and L. Field, *J. Am. Chem. Soc.*, **72,** 59 (1950). [c] V. N. Ipatieff, H. Pines, and B. S. Friedman, *J. Am. Chem. Soc.*, **60,** 2731 (1938). [d] S. Kenyon, H. Phillips, V. P. Pittman, R. B. Shackleton, D. E. Kahn, F. H. Yortson, and N. E. Cochinaras, *J. Chem. Soc.*, 1072 (1935). [e] F. Ashworth and G. N. Burkhardt, *J. Chem. Soc.*, 1791 (1928). [f] C. Finzi and V. Bellavito, *Gazz. Chim. Ital.*, **62,** 699 (1932). [g] E. Fromm, *Ber.*, **41,** 3397 (1908). [h] R. Brown, W. E. Jones, and A. R. Pinder, *J. Chem. Soc.*, 3315 (1951). [i] N. M. Kolbina, N. V. Bogoslovskii, G. A. Gartman, and I. I. Lapkin, *Zh. Org. Khim.*, **12,** 1708 (1976). [j] H. Hellmann and D. Eberle, *Justus Liebigs Ann. Chem.*, **662,** 188 (1963). [k] E. J. Corey and D. Seebach, *J. Org. Chem.*, **31,** 4097 (1966). [l] Not available.

are attached). The solvents for NMR samples were carbon tetrachloride and $CDCl_3$. Infrared spectra were obtained with a Beckman IR-33 spectrophotometer.

Boiling points and melting points are reported uncorrected. The latter were taken in open capillaries with a Büchi apparatus.

The olefins, as well as the other chemicals used, were products of Merck or Fluka, usually 98% pure or better, and they were used as such. Exceptions to this were 1,4-divinylbenzene, which contained approximately 50 mol % of *p*-ethylstyrene, and 2,4,4,6,6-pentamethyl-1-heptene (Fluka technical grade). The latter was distilled before use.

Benzyl phenyl sulfide was prepared from benzyl chloride and thiophenol in aqueous sodium hydroxide and recrystallized from methanol (see Table IV in supplementary material). Trityl phenyl sulfide was prepared from triphenylmethanol and thiophenol according to a published procedure.[11] *sec*-Butyl phenyl sulfide was prepared from *sec*-butyl bromide and thiophenol in aqueous NaOH. *tert*-Butyl and *tert*-amyl phenyl sulfides were synthesized according to the literature[11] from the corresponding chlorides. The carbinols, 1-(*p*-methoxyphenyl)ethanol, 1-(*m*-methylphenyl)ethanol, 1-(1-naphthyl)ethanol, and 1-(2-naphthyl)ethanol, were prepared from the corresponding ketones by sodium borohydride reduction and finally converted to the respective phenyl sulfides.[11]

Tetrahydrofuran was purified as described previously.[4]

Reactions of air-sensitive reactants and/or products were carried out under an atmosphere of argon. For details of reaction setups and workup procedures for carbonation mixtures, see the previous paper.[4]

1,1-Diphenylethyl Phenyl Sulfide. This procedure serves as an example of the reaction of an activated olefin with thiophenol and perchloric acid as catalyst. Under an atmosphere of argon was added by means of a pressure-equalizing addition funnel 36 g (0.2 mol) of 1,1-diphenylethylene to a stirred mixture of 23 mL of thiophenol and 1.0 mL of 70% perchloric acid (cooling, ice–water bath). At the end of the addition, cooling was discontinued and the mixture was stirred at room temperature for 2 h (6 h for the less activated olefins such as styrenes). Benzene (150 mL) was added followed by sodium hydroxide solution, and the resulting mixture was stirred for about 0.5 h. The benzene layer was separated and dried over anhydrous $MgSO_4$. Evaporation of the benzene in a rotary evaporator left a viscous oil which solidified on standing. It weighed 56.6 g, 98% of the theory. This material, after one recrystallization from hexane (90% recovery), melted at 36–38 °C. For NMR data, see Table IV (supplementary material).

2-Octyl Phenyl Sulfide. A mixture of 11 mL of thiophenol, 11.2 g (0.1 mol) of 1-octene, and 1.0 mL of 70% $HClO_4$ was heated at 95–100 °C and magnetically stirred for 2.5 h. The reaction mixture was allowed to cool to room temperature and then diluted with 100 mL of benzene. The benzene solution was washed with sodium hydroxide solution and water and dried over $MgSO_4$. Evaporation of benzene and vacuum distillation of the product gave 16.7 g (79%) of the title compound, boiling (0.15 mm) at 92 °C.

Table IV (supplementary material) summarizes some data of the new sulfides and Table V the boiling or melting points of the known sulfides.

Bis(phenylthio)methane. Methylene chloride, instead of the rather expensive methylene iodide,[18] was utilized in the following method. A mixture of anhydrous potassium carbonate (30 g), ethylene glycol (100 mL), methylene chloride (25 mL), and thiophenol (22 mL, ~0.2 mol) was stirred and heated to reflux (65–70 °C) for 3 h. At the end of this period of time, the reaction mixture was poured into a beaker containing 500 mL of water, the product was taken up in benzene (150 mL), and the benzene layer was washed with water and finally dried over $MgSO_4$. Evaporation of the benzene solution, after removing the drying agent, in a rotary evaporator left a liquid which on distillation under reduced pressure afforded 18.4 g (80%) of the title compound, boiling (0.2 mm) at 130–145 °C. This liquid, on refrigeration, solidified into a hard mass which melted at 35–36 °C. After one recrystallization from hexane, it melted at 38–39 °C (lit.[18] mp 39.5–40.5 °C).

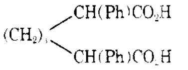
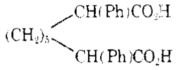
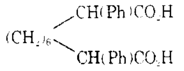
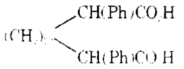
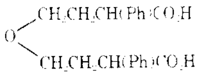
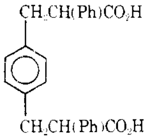
Metalation of Benzhydryl Phenyl Sulfide. A solution of 5.52 g (20 mmol) of Ph_2CHSPh in 25 mL of absolute THF was introduced into the reaction system in which an atmosphere of argon had been previously established. The reaction flask was surrounded with a mixture of dry ice and acetone, and 17 mL of 1.46 M (25 mmol) butyllithium in benzene was added with a syringe to the stirred sulfide solution. A red coloration appeared immediately. The resulting solution was stirred for 0.25 h at the bath temperature and then at room temperature for 19 h. Carbonation and conventional workup of the carbonation mixture afforded 6.0 g (93%) of 1,1-diphenyl-1-(phenylthio)acetic acid: neutralization equivalent 324, calcd 320. The recrystallized material from hexane melted at 121–123 °C. See Table VI for some data of new carboxylic acids.

Coupling of Lithiated Sulfides with Alkyl Bromides. The metalated sulfides PhCH(Li)SPh and $Ph_2C(Li)SPh$ were reacted with a small excess of a primary or secondary alkyl bromide. The reaction with the secondary bromides was markedly slower than the reaction with the primary ones. Reagent $(PhS)_2CHLi$ did not couple at all with secondary alkyl bromides. In reacting a dibromide with the reagent PhCH(Li)SPh, stoichiometric amounts of the reagents were used and the dibromide was added in small portions in order to avoid possible formation of the product $PhCH(SPh)(CH_2)_nBr$.

Reaction of *tert*-Butyl Phenyl Sulfide with Lithium Naphthalene. To a stirred solution of lithium naphthalene under argon, prepared from 13.0 g (~0.1 mol) of naphthalene, 0.70 g (0.1 g-atom) of lithium metal, and 100 mL of THF after 6 h of stirring at room temperature was added a solution of 8.3 g (50 mmol) of *tert*-butyl phenyl sulfide in 10 mL of THF at −60 to −50 °C. The resulting dark red solution was stirred for 0.5 h at −65 to −60 °C and then carbonated by pouring it rapidly into a beaker containing a slurry of crushed dry ice and anhydrous ether. From the carbonation mixture, after treatment with 30% hydrogen peroxide,[4] an acidic product was isolated by ether (3 × 150 mL) extraction. Evaporation of the ether, after drying over $MgSO_4$, left 8.0 g of solvent-free product with the characteristic odor of pivalic acid. NMR analysis of the mixture indicated the presence of a dihydronaphthalene derivative(s), resonance band at ~6.1 ppm, as well as bands due to *tert*-butyl groups. This mixture was subjected to steam distillation, giving a nonvolatile in-steam fraction (5.50 g, 48%) as *tert*-butyldihydronaphthoic acid and 2.2 g of pivalic acid, isolated by ether extraction from the distillate. Assuming that the difference of 0.3 g in material balance is due to loss of pivalic acid during separation, the yield of pivalic acid is estimated to be 49%.

Cleavage of *tert*-Butyl Phenyl Sulfide with Lithium Dispersion in THF. Employing the system described in the previous paper,[4] a mixture of 1.0 g of mineral oil free lithium dispersion, 4.15 g (25 mmol) of *t*-BuSPh, and 50 mL of absolute THF under argon was

Table VI. Data of New Carboxylic Acids

carboxylic acid	registry no.	mp or bp (mm), °C	NMR, ppm
 $(CH_2)_3\genfrac{}{}{0pt}{}{CH(Ph)CO_2H}{CH(Ph)CO_2H}$	68602-52-8	147–149 (toluene)	1.27 (br m, 2 H, CCH_2C), 1.90 (br m, 4 H, CH_2CPH), 3.56 (t, $J \simeq 7.0$ Hz, CHPh), 7.30 (s, 10 H, 2Ph)
 $(CH_2)_5\genfrac{}{}{0pt}{}{CH(Ph)CO_2H}{CH(Ph)CO_2H}$	31161-73-6	glassy	1.26 (br s, 6 H, $C(CH_2)_3C$), 1.88 (br m, 4 H, CH_2CPh), 3.55 (br t, $J = 7.5$ Hz, 2 H, CHPh), 7.32 (s, 10 H, 2Ph)
 $(CH_2)_6\genfrac{}{}{0pt}{}{CH(Ph)CO_2H}{CH(Ph)CO_2H}$	68602-53-9	150–156 (fast) (C_6H_6) 150–160 (slow) (C_6H_6)	1.26 (br s, 8 H, $C(CH_2)_4C$), 1.91 (br m, 4 H, CH_2CPh), 3.57 (t, J = 7.5 Hz, 2 H, CHPh), 7.35 (s, 10 H, 2Ph)
 $(CH_2)_{10}\genfrac{}{}{0pt}{}{CH(Ph)CO_2H}{CH(Ph)CO_2H}$	68602-54-0	113–116 (C_6H_6)	1.24 (br s, 16 H, $C(CH_2)_8C$), 1.91 (br m, 4 H, CH_2CPh), 3.60 (t, $J \simeq 8$ Hz, 2 H, CHPh), 7.36 (s, 10 H, 2Ph)
 $O\genfrac{}{}{0pt}{}{CH_2CH_2CH(Ph)CO_2H}{CH_2CH_2CH(Ph)CO_2H}$	68602-55-1	visc. liquid	1.65–2.84 (br almost structureless band), 3.37 (diffuse unsymmetric t), 3.85 (diffuse unsymt, 10 H, aliphatic), 7.30 (s, 10 H, 2Ph)
	68602-56-2	216–221 (EtOH–hexane)	100-MHz spectrum (CD_3COCD_3) 2.97 (unsym quart) and 3.35 (unsym quart) (4 H, $ArCH_2C$), 3.92 (unsym quart, 2 H, $CCHCO_2$), 7.08 (s) and 7.33 (s) (14 H, aromatic)
$Ph_2C(SPh)CO_2H$	18626-37-4	121–123 (hexane)	unsym triplet-like multiplet with peaks at 7.11, 7.28, and 7.45 (15 H, 3Ph), 11.0 (s, 1 H, acidic)

stirred (Hershberg stirrer) at −50 to −40 °C for 2 h. The yellowish solution on carbonation (H_2O_2 workup) afforded 1.98 g (78%) of pivalic acid.

(1,1-Diphenyl-2-methylbutyl)lithium. A solution of 2.85 g (8.5 mmol) of 1,1-diphenyl-2-methylbutyl phenyl sulfide in 10 mL of THF was added with a syringe to a stirred solution (1.0 M, 18 mL) of lithium naphthalene under argon at −65 to −40 °C. The mixture turned red immediately. Stirring was continued for about 1 h at −60 to −40 °C in order to ensure the complete reaction of the precipitated lithium naphthalene caused by cooling. Carbonation (dimethyl sulfate workup[4]) gave 2.10 g (92%) of 2,2-diphenyl-3-methylpentanoic acid, mp 147–149 °C from hexane (lit.[19] mp 151 °C).

(1,1-Diphenylethyl)sodium. Sodium metal (1.3 g, 56 mg-atom) was dispersed in 50 mL of dry toluene by adding 0.3 mL of chlorobenzene to the vigorously stirred sodium melt at the temperature of refluxing toluene. By this method a very fine particle size can be achieved by stirring the melt for a few seconds only, and the dispersion does not tend to aggregate easily. When the flask cooled down to room temperature, the supernatant toluene was siphoned out and replaced by 50 mL of THF in which 5.8 g (20 mmol) of 1,1-diphenylethyl phenyl sulfide had been dissolved. On stirring, an orange coloration appeared immediately. The mixture was stirred rapidly for 2 h while cooling the flask with a cold water bath. Carbonation and H_2O_2 workup afforded 4.0 g (89%) of 2,2-diphenylpropionic acid, isolated by filtration from the acidified carbonation water layer. This product melted at 170–172 °C after one recrystallization from hexane–benzene (lit.[20] mp 173–174 °C).

(3-Lithiooxy-1-phenylpropyl)lithium. To a solution of 20 mmol of lithium naphthalene in 30 mL of THF under argon was added a solution of 2.05 g (5 mmol) of benzhydryl 3-phenyl-3-(phenylthio)propyl ether in 10 mL of THF at −75 to −45 °C with stirring. The reaction appeared to have gone to completion on mixing the reagents. After stirring the mixture for 0.25 h at about −60 °C, it was carbonated. From the carbonation mixture, after treatment with Me_2SO_4, etc., the acidic products were isolated by ether extraction (4 × 150 mL). A 1.88-g (98%) yield of an almost equimolar mixture of diphenylacetic acid and 4-hydroxy-2-phenylbutanoic acid was obtained as shown by NMR analysis. In order to ascertain the structure of the latter acid, it was synthesized by an independent synthesis. The ether acid, $PhCH(CO_2H)CH_2CH_2OCHPh_2$, was prepared[21] first. This derivative had the following properties. After recrystallization from ethyl acetate–hexane, it melted at 100–102 (fast) and 98–106 °C (slow): NMR ($CDCl_3$), diffuse m centered at 2.33 ppm (2 H, Ph–C–CH_2–C–O), multiplet extending from ~3.25 to 4.40 ppm (3 H, –CH–CO_2 + –CH_2–O), 5.28 (s, 1 H, Ph–CH–Ph), 7.31 (s, 15 H, 3Ph) ppm.

The ether acid was cleaved by lithium in THF and in the presence of a catalytic amount of naphthalene to a mixture of $PhCH(CO_2Li)CH_2CH_2OLi$ and Ph_2CHLi. After hydrolysis of this mixture, the hydroxy acid was isolated as an oil: NMR ($CDCl_3$) 2.48 (m, 2 H, Ph–C–CH_2–C–O), 3.79 (q, 1 H, Ph–CH–CO_2), 4.33 (septet, 2 H, –CH_2–O), 7.0 (br s, 1 H, –OH), 7.35 (s, 5 H, aromatic) ppm.

Reaction of 1,2-Diphenyl-1-lithiooxy-2-(phenylthio)ethane with 4 equiv of Lithium Naphthalene. To a solution of 1.84 g (6.0 mmol) of 1-hydroxy-2-(phenylthio)bibenzyl in 15 mL of THF under argon was added 3.5 mL of a 1.70 M solution of BuLi in benzene at −60 to −30 °C, followed by the addition of 25 mmol of lithium naphthalene as an 0.8 M solution in THF at −60 to −45 °C. The reaction appeared to have gone to completion on mixing the reagents (3–5 min). The resulting brownish solution was stirred for 0.25 h at about −60 °C and then carbonated. From the carbonation mixture, after H_2O_2 treatment, etc., 1.35 g (84%) of *meso*-diphenylsuccinic acid was isolated, mp 245 °C, after one recrystallization from ethyl acetate–hexane (lit.[22] mp 242–245 °C). As an additional confirmation of the structure of the acid, stilbene was converted to the dianion by excess lithium metal in THF and subsequently carbonated. A quantitative yield of *meso*- (mainly) and *dl*-diphenylsuccinic acid was obtained. The component soluble in boiling AcOEt, from which it precipitated by adding hexane, melted at 233–237 °C. This material and the acid isolated from the hydroxy sulfide run exhibited identical IR spectra in every detail. The component insoluble in boiling ethyl acetate melted at 273–280 °C, and it is presumed to be the racemic form.

Acknowledgment. We would like to thank Mrs M. Voyadji and Miss M. Avgerinou for technical assistance.

Registry No.—*meso*-Diphenylsuccinic acid, 1225-13-4; *tert*-amyl chloride, 594-36-5; lithium naphthalene, 7308-67-0.

Supplementary Material Available: Data of new sulfides (Table IV) (4 pages). Ordering information is given on any current masthead page.

References and Notes

(1) (a) B. J. Wakefield, "The Chemistry of Organolithium Compounds", Pergamon Press, Oxford, 1974, p 21; (b) G. E. Coates, M. L. H. Green, and K. Wade, "Organometallic Compounds", Vol. 1, Mathuen and Co. Ltd., London, 1969, p 6.
(2) Reference 1a, pp 26–50; ref 1b, p 17.
(3) K. Ziegler and H. Dislich, *Chem. Ber.*, **90,** 1107 (1957).
(4) C. G. Screttas and M. Micha-Screttas, *J. Org. Chem.*, **43,** 1064 (1978).
(5) Ethers are cleaved by organolithium reagents; see, e.g., S. C. Honeycutt, *J. Organomet. Chem.*, **29,** 1 (1971), R. B. Kroposki and D. E. Potter, *J. Org. Chem.*, **37,** 560 (1972); A. Maerker and W. Demouth, *Angew. Chem., Int. Ed. Engl.*, **12,** 75 (1973); G. Köbrich and A. Baumann, *ibid.*, **12,** 856 (1973).
(6) An interesting type of molecular fragmentation was encountered during the reaction of "tributylene" with thiophenol:

$$(CH_3)_3CCH_2C(CH_3)_2CH_2C(CH_3){=}CH_2 \xrightarrow{H^+ClO_4^-} (CH_3)_3CCH_2C(CH_3)_2CH_2(CH_3)_3C^+ \longrightarrow$$

$$(CH_3)_3CCH_2C(CH_3){=}CH_2 + t\text{-Bu}^+ \xrightarrow{PhSH} t\text{-BuSPH} + t\text{-BuCH}_2C(CH_3)_2SPh$$

For analogous processes, see, e.g., D. Bethell and V.Gold, "Carbonium Ions an Introduction", Academic Press, London, 1967, p 200.

(7) J. F. Garst, in "Free Radicals", J. K. Kochi, Ed., Wiley, New York, 1973, p 503.

(8) G. D. Sargent and G. A. Lux, *J. Am. Chem. Soc.*, **90**, 7160 (1968).

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Carbonyl Transposition Studies

Ying K. Yee and Arthur G. Schultz*

Department of Chemistry, Cornell University, Ithaca, New York 14853

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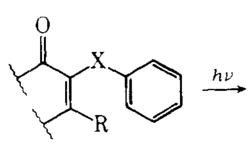
In a program directed toward the total synthesis of the *Amaryllidaceae* alkaloid lycoramine **1**, the model photoconversion **2** → **3** and the 1,2-carbonyl transposition **3** → **4** were studied in detail. Various methods for carbonyl transposition based on a favorable direction of enolization and kinetic enolate formation in **3** were explored. The most effective method in this system, as well as in the actual synthesis of *dl*-lycoramine, involves bissulfenylation of the kinetic enolate of **3** with phenyl phenylthiosulfonate to give thioketal ketone **17**, reduction of **17** to hydroxy thioketal **18a**, conversion of **18a** to thioketal mesylate **18c**, thioketal hydrolysis to give keto mesylate **14c**, and finally reductive cleavage of **14c** with chromous chloride in aqueous acetone at 25 °C to give **4** in 58% overall yield from **3**. Alternatively, hydroxy thioketal **18a** gives ketol **14b** (as a single tautomer), which is converted to keto mesylate **14c** and thence to **4** in 66% isolated yield from **3**.

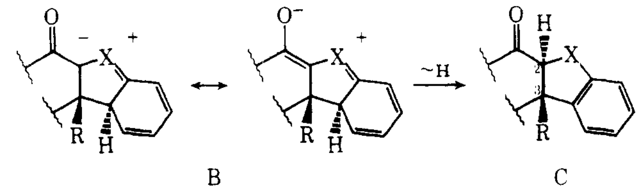
We have demonstrated that photocyclization–rearrangement (heteroarom directed photoarylation) of aryl vinyl heteroatom systems is an extremely flexible method for carbon–carbon bond formation to an aromatic nucleus (e.g., A → B → C).[1] The heteroatoms oxygen, sulfur, selenium, and nitrogen can be employed and a wide variety of functional groups are compatible with the conditions for photocyclization. Furthermore, a high degree of stereochemical control is possible (e.g., at C(2) and C(3) in C),[2] and an important application of the photoreaction is the bonding of an aromatic ring to an angular carbon atom located at a ring junction.[3]

Early in our studies, we discovered that while simple aryl vinyl ethers undergo inefficient photocyclization, excellent chemical and photochemical cyclization yields are obtained with 2-aryloxyenones (A, X = oxygen). The carbonyl group in A establishes a chromophore (enone), with which relatively low energy Pyrex-filtered light may be employed and at the same time presumably provides for stabilization of the intermediate ylide B as shown.

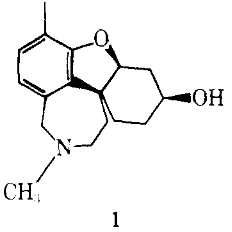
As a result of an intended application of heteroatom directed photoarylation to a total synthesis of the *Amaryllidaceae* alkaloid lycoramine **1**, we became interested in the model photoconversion **2** → **3** and the 1,2-carbonyl transposition **3** → **4**. In this paper, we present a detailed study of carbonyl transposition in **3**. This report should be of general synthetic interest, because for the first time, a variety of



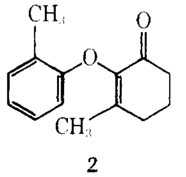
A



B C

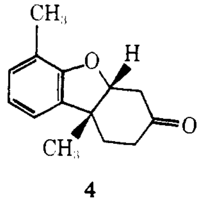


1

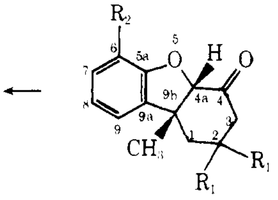


2

hν, ROH



4



3, $R_1 = H$; $R_2 = CH_3$
3a, $R_1 = CH_3$; $R_2 = H$

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* Direct correspondence to this author at the Department of Chemistry, Rensselaer Polytechnic Institute, Troy, New York 12181.

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