1064 *J. Org. Chem., Vol. 43, No. 6, 1978* Screttas and Micha-Screttas

Hydrolithiation of α-Olefins by a Regiospecific Two-Step Process. Transformation of Alkyl Phenyl Sulfides to Alkyllithium Reagents

Constantinos G. Screttas* and Maria Micha-Screttas

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

Received April 4, 1977

The cleavage of primary alkyl phenyl sulfides by lithium naphthalene or lithium dispersion in tetrahydrofuran has been studied. Cleavage takes place in the direction of alkyllithium and lithium thiophenoxide. Preparation of alkyl phenyl sulfides by the anti-Markownikoff addition of thiophenol to α-olefins and subsequent cleavage by lithium led to the regiospecific addition of the elements of lithium hydride to the olefinic double bond. The overall yields of the alkyllithium products ranged from 40 to 90%. The preparation of a number of new mono- and dilithium organometallics is reported, some of which bear functional groups, e.g., $O(CH_2CH_2CH_2Li)_2$, $PhCH_2O(CH_2)_nLi$ (n = 3, 4), and $PhS(CH_2)_nLi$ (n = 3, 4, 5, 6).

The cleavage of a carbon–halogen bond by lithium metal is certainly the method of choice in preparative organolithium chemistry.[1] However, other heteroatoms bonded to carbon exhibit to a varying extent the same tendency to undergo cleavage[2] by lithium or other alkali metals and give products containing metal bonded to carbon. Ethers,[3,4] sulfides,[5] phosphines,[6] and several other classes of organic compounds are known to undergo cleavage by alkali metal, dissolving metals, or aromatic radical anions.[7] In very few cases, however, such reactions have found some utility in organometallic synthesis. For example, the preparation of benzyllithium,[3b] allyllithium,[4] and 2-phenylisopropylpotassium[8] utilizes the facile cleavage of benzyl, allyl, and 2-phenylisopropyl methyl ethers, respectively.

It has been proposed[9] that the cleavage of alkyl aryl ethers follows a three-step sequence involving two single electron transfer steps

$$\mathrm{ArOR} \xrightarrow{+e^-} (\mathrm{ArOR})^{-}\cdot \longrightarrow \mathrm{ArO}^- + \mathrm{R}^\cdot \xrightarrow{+e^-} \mathrm{ArO}^- + \mathrm{R}^- \quad (1)$$

When the reaction takes place at sufficiently low temperature, the fission of the radical anion $(ArOR)^{-}\cdot$ is mainly controlled by thermodynamic rather than kinetic factors, and in such a case the product-determining step is the one in which the most stable anion and the most stable radical are to be produced. Thus, alkyl aryl ethers tend to cleave to the phenoxide anion and alkyl carbanion.[9] It appears that the reaction is dominated by the stability of the phenoxide, since it is derived from a relatively strong acid; pK_a for phenol = 10. The alternative mode of cleavage which would lead to the formation of the alkoxide, pK_a of an alcohol usually around 18, and phenyl radical appears to have unfavorable energetics.

Along this line of reasoning the group PhS– would be expected to be a better leaving group than phenoxide in the cleavage of alkyl phenyl sulfides; pK_a of thiophenol = 6.5. Indeed, the group PhS– behaves sometimes as a pseudohalogen.[10] Besides its ready cleavage by alkali metals, which is reminiscent of halogen-like behavior, thiophenol is closely analogous to HBr as far as its mode of addition to an olefinic double bond in the presence of peroxide[11] is concerned.

The purpose of this paper is to demonstrate that the constituents of lithium hydride can be added regiospecifically to α-olefins by a two-step reaction sequence. The direct addition of lithium hydride to an olefin would certainly be a decisive step toward the solution of the problem of total synthesis of organolithium reagents. This goal, however, might prove to be a difficult task, due to lack of solubility of LiH in the usual aprotic solvents. The results given in the following section demonstrate that an alternative indirect "hydrolithiation" can be achieved in two steps, giving regiospecifically the primary organolithium compound. This method exploits two reactions, each of which is usually of high yield, namely, (1) the free-radical addition of thiphenol to α-olefins and (2) the cleavage of the C–S bond by lithium metal or lithium arenides, in a reaction which leads to the formation of organometallic products.

$$\mathrm{RCH{=}CH_2 + PhSH \xrightarrow{peroxide} RCH_2CH_2SPh}$$

$$\mathrm{RCH_2CH_2SPh + 2Li \rightarrow RCH_2CH_2Li + PhSLi} \quad (2)$$

Until the direct addition of lithium hydride to olefins becomes feasible the above alternative could be useful in certain cases in preparative organolithium chemistry.

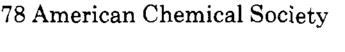
Results and Discussion

In Table I are summarized the yields of the sulfides obtained by the AIBN or photochemically induced addition of thiophenol to various olefins, including a few with functional groups. The yields of the corresponding alkyllithiums by the method of lithium naphthalene and of lithium dispersion are also included in the table.

Particularly facile is the addition of thiophenol to activated olefins such as styrene, 1,1-diphenylethylene, and diallyl ether. Generally, the yields of the distilled sulfides range from good to excellent.

Alkyl phenyl sulfides undergo a rather facile cleavage by lithium naphthalene in tetrahydrofuran (THF) solvent. Of course, the cleavage reaction must be carried out at low enough temperature in order to prevent organolithium loss by THF cleavage.[12] Even at temperatures as low as −70 °C RSPh and $Li^+C_{10}H_8^-\cdot$ react at an appreciable rate. Generally, accumulation of phenyl groups in the sulfide molecule increases the ease of cleavage of the sulfide.[13] This might well mean that the higher the electron affinity of the sulfide the more facile the cleavage.[14] Thus a sulfide such as n-octyl phenyl cleaves considerably less readily than Ph_2CHCH_2SPh for example. It appears that sulfides behave like their oxygen counterparts[9] as far as the reaction with aromatic radical ions is concerned. The rate-determining step in most cases[14] is the transfer of the odd electron from the aromatic radical ion to the sulfide, a process which, of course, is governed by the relative electron affinities of the aromatic hydrocarbon and the sulfide.[15a] Reaction times usually range between 0.1 and 0.5 h at temperatures from −55 to −20 °C.

Our expectations about the leaving aptitude of the thiophenoxy group have not been disappointed. Cleavage occurred according to the expected mode (eq 3) and the yields of the



$$\mathrm{RSPh} + 2\,\mathrm{Li^+C_{10}H_8^-\cdot} \begin{cases} \not\longrightarrow \mathrm{PhLi + RSLi} \\ \longrightarrow \mathrm{RLi + PhSLi} \end{cases} \quad (3)$$

0022-3263/78/1943-1064$01.00/0

Table I. Two-Step Hydrolithiation of Some Olefins

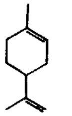
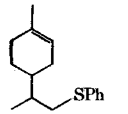
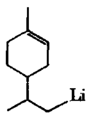
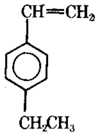
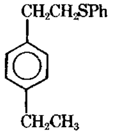
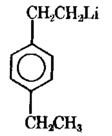
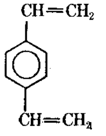
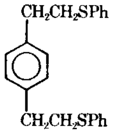
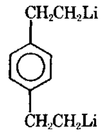
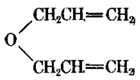
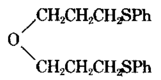
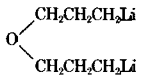
Olefin	Registry no.	Sulfide (% yield)	Registry no.	Alkyllithium	Registry no.	% yield of RLi by	
						$Li^+C_{10}H_8^{-\cdot}$	Li dispersion
$CH_3(CH_2)_4CH{=}CH_2$	592-76-7	$CH_3(CH_2)_6SPh$ (72)	13910-15-1	$CH_3(CH_2)_6Li$	25047-67-0	87	62
$CH_3(CH_2)_5CH{=}CH_2$	111-66-0	$CH_3(CH_2)_7SPh$ (78)	13910-16-2	$CH_3(CH_2)_7Li$	3314-49-6	93	61
$CH_3(CH_2)_3C(Et){=}CH_2$	1632-16-2	$CH_3(CH_2)_3CH(Et)CH_2SPh$ (67)	13910-17-3	$CH_3(CH_2)_3CH(Et)CH_2Li$	13067-81-7	61	70
$(CH_3)_3CCH{=}CH_2$	558-37-2	$(CH_3)_3CCH_2CH_2SPh$ (60)	15672-95-4	$(CH_3)_3CCH_2CH_2Li$	6909-52-0	100	80
$PhCH_2CH{=}CH_2$	300-57-2	$Ph(CH_2)_3SPh$ (80)	30134-12-4	$Ph(CH_2)_3Li$	64740-46-1	70	79
$PhCH_2CH_2CH{=}CH_2$	768-56-9	$Ph(CH_2)_4SPh$ (83)	64740-40-5	$Ph(CH_2)_4Li$	64740-47-2		74
	138-86-3	 (70)	64740-41-6		64740-48-3	74	55
$PhCH{=}CH_2$	100-42-5	$PhCH_2CH_2$ SPh (95)	13865-49-1	$PhCH_2CH_2Li$	42808-98-0	83	65
$PhC(CH_3){=}CH_2$	98-83-9	$PhCH(CH_3)CH_2SPh$ (94)	4148-81-6	$PhCH(CH_3)CH_2Li$	64740-49-4	82	89
	3454-07-7	 (>90)	64740-42-7		64740-50-7	71	80
	105-06-6	 (>90)	64740-43-8		64740-51-8	100	94
$Ph_2C{=}CH_2$	530-48-3	Ph_2CHCH_2SPh (100)	13112-47-5	Ph_2CHCH_2Li	64740-52-9	96	87
$PhCH_2OCH_2CH{=}CH_2$	14593-43-2	$PhCH_2O(CH_2)_3SPh$ (70)	64740-44-9	$PhCH_2O(CH_2)_3Li$	64740-53-0	70	
	557-40-4	 (100)	64740-45-0		64740-54-1	88	90
$ClCH_2CH{=}CH_2$	107-05-1	$Cl(CH_2)_3SPh$ (70)	4911-65-3	$PhS(CH_2)_3Li$	64740-55-2	59	

Table II. Transformation of Certain Sulfides, Bearing a Second Functional Group, to Substituted Alkyllithiums

Starting material	Registry no.	Sulfide (% yield)	Registry no.	Alkyllithium	Registry no.	% yield
$ClCH_2CH_2Cl$; PhSH	107-06-2; 108-98-5	$PhSCH_2CH_2SPh$ (90)	622-20-8	$PhSCH_2CH_2Li$	64740-26-7	0
$Cl(CH_2)_4Cl$; PhSH	110-56-5; -	$Cl(CH_2)_4SPh$ (65)		$PhS(CH_2)_4Li$	64740-27-8	75
$Cl(CH_2)_5Cl$; PhSH	628-76-2; -	$Cl(CH_2)_5SPh$ (70)	14633-28-4	$PhS(CH_2)_5Li$	64740-28-9	66
$Cl(CH_2)_6Cl$; PhSH	2163-00-0; -	$Cl(CH_2)_6SPh$ (75)	64740-56-3	$PhS(CH_2)_6Li$	64740-29-0	62
$Cl(CH_2)_4SPh$; PhOH	14633-31-9; 108-95-2	$PhO(CH_2)_4SPh$ (93)	59950-11-7	$PhO(CH_2)_4Li$	64740-30-3	83
$Cl(CH_2)_4SPh$; $PhCH_2OH$	-; 100-51-6	$PhCH_2O(CH_2)_4SPh$ (53)	64740-57-4	$PhCH_2O(CH_2)_4Li$	64740-31-4	61
$Cl(CH_2)_4Cl$; PhSH		$PhS(CH_2)_4SPh$ (95)	5330-89-2	$PhS(CH_2)_4Li$		80
$Br(CH_2)_5Br$; PhSH	111-24-0; -	$PhS(CH_2)_5SPh$ (90)	40340-02-1	$PhS(CH_2)_5Li$		75
$Cl(CH_2)_6Cl$; PhSH		$PhS(CH_2)_6SPh$ (90)	55129-89-0	$PhS(CH_2)_6Li$		65
Ph_3CH; $BrCH_2CH_2SPh$	519-73-3; 4837-01-8	$Ph_3CCH_2CH_2SPh$ (81)	64740-24-5	Ph_3CLi	733-90-4	54
Ph_2CH_2; $BrCH_2CH_2SPh$	101-81-5; -	$Ph_2CHCH_2CH_2SPh$ (79)	64740-25-6	Ph_2CHLi	881-42-5	88

alkyllithium reagents ranged in most cases from 70 to 100%. Yields and product characterization were based on the carboxylic acids produced by carbonation of the alkyllithium compounds.

Considerably less ready is the cleavage of the sulfides with lithium metal in THF. The use of lithium dispersion and a catalytic amount of naphthalene, especially in conjuction with the employment of a Hershberg stirrer, was found to be a useful method. In this case, however, reaction times of 1–3 h are required at temperatures from −40 to −20 °C. This inconvenience is offset by the absence of naphthalene in the products. Organolithium yields by the method of lithium dispersion ranged from 55 to 94%. It must be noted that the cleavage reaction of a given sulfide by the two methods was not run at the same temperature and therefore any conclusions drawn on the basis of the two sets of yields could be risky.

Thiophenol and naphthalene could be a problem in product isolation when the organolithium prepared by this method is used to make a derivative other than a carboxylic acid. Acidic derivatives can be separated from thiophenol by oxidizing the latter to the corresponding disulfide, PhSSPh, with alkaline hydrogen peroxide. Another way of converting thiophenol to a neutral, less malodorous derivative is by reacting it with dimethyl sulfate, i.e., by converting it to thioanisole. The separation of a neutral product from naphthalene could be a more serious problem. Naphthalene is very volatile in steam, and steam distillation should be the method of choice for separating naphthalene from a neutral product whenever possible. We did not experience any difficulties in separating naphthalene from alkyldiphenylcarbinols by steam distillation.

Complications could arise in the sulfide cleavage reaction in cases where other reactive sites are present in the sulfide molecule, for example, the presence of an acidic C–H bond,[15b] in which self-metalation can take place:

$$\mathrm{ArCH_2SPh + 2Li \rightarrow ArCH_2Li + PhSLi}$$

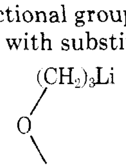
$$\mathrm{ArCH_2Li + ArCH_2SPh \rightarrow ArCH(Li)SPh + ArCH_3}$$

Although this situation does not occur in the case of the sulfides prepared by the anti-Markownikoff addition of thiophenol to olefins, it can happen in cleavage of sulfides prepared by other methods. The presence of other cleavable groups such as halogen-carbon, PhO–C, Ph_2P–C, and others could make the reaction complicated. The order, however, of cleavability according to our results is Cl–C > PhS–C > PhO–C > Ph_2P–C, an order that varies inversely with the acid pK_a values of HCl, PhSH, PhOH, and Ph_2PH, respectively: −6.1; 6.5; 9.99; 21.7.[16]

The marked difference in the cleavability of halogen vs. thiophenoxy and thiophenoxy vs. phenoxy or alkoxy group made possible the preparation of some organolithium reagent containing the functional groups of ether or thioether, such as **1**–**4**. The results with substituted alkyllithiums are summarized in Table II (see also the last three entries of Table I). Alkoxy sulfides and chlorosulfides or disulfides have been employed in the preparation of the substituted organolithium reagents, some of which are new. Regioselectivity in cleaving one of the two cleavable groups has been achieved by employing inverse addition and just 2 equiv of lithium naphthalene and a low reaction temperature, usually between −70 and −65 °C. Disulfides of the general structure $PhS(CH_2)_nSPh$ can be transformed to $PhS(CH_2)_nLi$ under the above mentioned conditions in a relatively clean reaction. It appears that lithium as a substituent exerts a deactivating effect upon the PhS–C in $PhS(CH_2)_nLi$ toward cleavage. This becomes evident from the longer reaction time which is required for complete reaction of a disulfide with 4 equiv of lithium naphthalene. Under this stoichiometry disulfides react with lithium naphthalene in a complicated manner. Besides the formation of dilithium derivative $Li(CH_2)_nLi$, the main reaction pathway appears to lead to the formation of species derived from the attack of the "radical anion" (**5**) on naphthalene radical anion.

$PhCH_2O(CH_2)_nLi$

1, $n = 3, 4$



2

$PhS(CH_2)_nLi$

3, n = 3–6

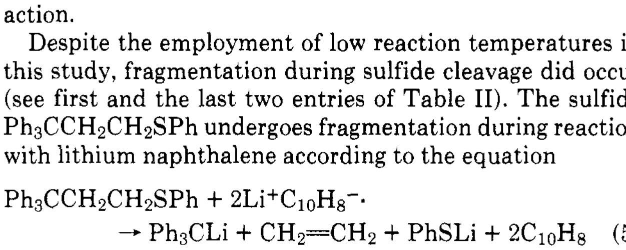
$PhO(CH_2)_4Li$

4

$$\mathrm{LiCH_2(CH_2)_{\mathit{n}-2}CH_2\cdot}$$

5

It could be of interest to contrast the different courses that are followed when 3-chloropropyl phenyl sulfide is reacted with sodium metal in refluxing toluene[17] and with lithium naphthalene in THF at −65 °C (eq 4). It is quite possible that under the homogeneous conditions fragmentation of the chloro sulfide is avoided due to the lower temperature of reaction.



(4)

Despite the employment of low reaction temperatures in this study, fragmentation during sulfide cleavage did occur (see first and the last two entries of Table II). The sulfide $Ph_3CCH_2CH_2SPh$ undergoes fragmentation during reaction with lithium naphthalene according to the equation

$$\mathrm{Ph_3CCH_2CH_2SPh + 2Li^+C_{10}H_8^{-}\cdot \rightarrow Ph_3CLi + CH_2{=}CH_2 + PhSLi + 2C_{10}H_8} \quad (5)$$

This fragmentation is closely analogous to the one observed during reduction of $Ph_3CCH_2CH_2I$ with sodium in liquid ammonia.[18] The sulfides $Ph_2CHCH_2CH_2SPh$ and $PhSCH_2CH_2SPh$ appear to belong to the same category. They too undergo fragmentation and form ethylene during reaction with lithium naphthalene. In the case of the sulfide $Ph_2CHCH_2CH_2SPh$, the extrusion of ethylene was inferred not only on the basis of the observed product Ph_2CHLi but also on the actual trapping of ethylene by cyclohexyllithium[19]

$$\mathrm{Ph_2CHCH_2CH_2SPh \xrightarrow[-PhSLi]{+2Li^+C_{10}H_8^{-}\cdot} Ph_2CHLi + CH_2{=}CH_2}$$
$$\xrightarrow{\mathrm{c\text{-}C_6H_{11}Li}} \longrightarrow \mathrm{Ph_2CHLi + c\text{-}C_6H_{11}CH_2CH_2Li} \quad (6)$$

A reasonable mechanism of these fragmentations is depicted in Scheme I. Of course, one can give several other

Scheme I

$$\mathrm{ZCH_2CH_2SPh + Li^+C_{10}H_8^{-}\cdot \rightleftharpoons (ZCH_2CH_2SPh)^{-}\cdot Li^+ + C_{10}H_8}$$

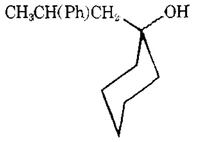
$$\mathrm{(ZCH_2CH_2SPh)^{-}\cdot Li^+ \rightarrow ZCH_2CH_2\cdot + PhSLi}$$

$$\mathrm{ZCH_2CH_2\cdot \rightarrow Z\cdot + CH_2{=}CH_2}$$

$$\mathrm{Z\cdot + Li^+C_{10}H_8^{-}\cdot \rightarrow Z^{-}Li^+ + C_{10}H_8}$$

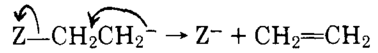
$$\mathrm{Z = Ph_3C, Ph_2CH, PhS}$$

Table III. Reaction of Select Organolithium Reagents with Ketones

Organolithium	Ketone	Registry no.	Carbinol	Registry no.	Yield, %	Mp, °C	NMR data
$CH_3CH(Ph)CH_2Li$	$Ph_2C{=}O$	119-61-9	$Ph_2C(OH)CH_2CH(Ph)CH_3$	64740-32-5	68	90–92	1.20 (d, J = 6.0 Hz, 3 H, CH_3); 1.87 (s, 1 H, OH); 2.8 (m, 3 H, $CHCH_2$); 7.25 (m, 15 H, three C_6H_5)
$CH_3(CH_2)_7Li$	$Ph_2C{=}O$		$CH_3(CH_2)_7C(OH)Ph_2$	16727-37-0	76	oil	0.87 (distort t, 3 H, CH_3); 1.25 (s, 12 H, $C(CH_2)_6C$); 2.17 (br s, 3 H, CH_2OH); 7.30 (m, 10 H, two C_6H_5)
$PhS(CH_2)_5Li$	$Ph_2C{=}O$		$PhS(CH_2)_5C(OH)Ph_2$	64740-33-6	33	oil	1.40 (br band, like a diffuse t, 6 H, $C(CH_2)_3C$); 2.15 diffuse t, 2 H, CH_2CO); 2.82 (diffuse t, 2 H, CH_2S); 3.36 (s, 1 H, OH); 7.25 (m, 15 H, three C_6H_5)
$CH_3CH(Ph)CH_2Li$	Cyclohexanone	108-94-1		64740-34-7	22	oil	1.26 (d); 0.89–2.02 (br band); 1.81 (q, ˀ 15 H); 3.02 (br m, 2 H, CHPh and OH); 7.25 (s, 5 H, aromatic)
Ph_2CHCH_2Li	$Ph_2C{=}O$		$Ph_2CHCH_2C(OH)Ph_2$	64740-35-8	38	92–94[a]	1.90 (s, 1 H, OH); 3.15 (d, J = 7.0 Hz, 2 H, CH_2CO); 4.04 (t, 1 H, CHPh); 7.15 (m, 20 H, four C_6H_5)

[a] Lit. mp 95–96 °C ("Dictionary of Organic Compounds", Vol. 5, Eyre and Spottiswoode, London, 1965, p 3034).

schemes which can rationalize the observed chemistry in these fragmentations. For example, the radical $ZCH_2CH_2\cdot$ alternatively can be reduced to the corresponding carbanion and then fragment:[18]



$$Z{-}CH_2CH_2^- \rightarrow Z^- + CH_2{=}CH_2$$

There could be not doubt that the driving force for these fragmentations is the thermochemical stability of the fragments.[20,21]

As far as the derivatization of the organolithium reagents prepared by the method described in this paper is concerned, it can be said that carbonation is the reaction which works quite well in all cases. A small number of select organolithium reagents were reacted with benzophenone or cyclohexanone. These results are summarized in Table III. Simple alkyllithium reagents such as *n*-octyl and 2-phenylpropyl gave good yields of carbinols after reaction with benzophenone. All reaction mixtures from the organolithium reagents and benzophenone were blue and paramagnetic. In the particular case of 2-phenylpropyllithium and benzophenone a 15% conversion of benzophenone to the corresponding ketyl could be estimated on the basis of the bulk paramagnetism of the solution. The low yield of the carbinol with the substituted organolithium $PhS(CH_2)_5Li$ could be due to the possible fragmentation of the $PhS(CH_2)_5$ moiety during reaction with benzophenone. Tetrahydrofuran is a notorious solvent for reactions of organolithium reagents with ketones having enolizable hydrogen(s). It appears that enolization was the main reaction between 2-phenylpropyllithium and cyclohexanone, judging from the low yield of the addition product. Lastly, the utility of these organolithium reagents for making derivatives other than carboxyclic acids remains to be determined.

Conclusion

It has been shown that alkyl phenyl sulfides prepared by the anti-Markownikoff addition of thiophenol to compounds bearing an α double bond between carbon atoms or almost any primary alkyl phenyl sulfide can be transformed to the corresponding alkyllithium reagents in yields ranging from fair to excellent. In contrast to the conventional alkyllithium preparation, which depends on the availability of the corresponding alkyl chlorides or bromides, the method described in this paper utilizes cheaper and more readily available starting materials, i.e., olefins. For example, the preparation of 2-phenylpropyllithium according to the conventional method would require 2-phenylpropyl chloride, a compound which is not listed in the catalogues of the major chemical suppliers, whereas the present method utilizes the very cheap α-methylstyrene. Shortcomings of the method could be: (1) the fact that one has to work with a malodorous reagent, thiophenol; (2) problems in product isolation due to the presence of naphthalene and thiophenol in the reaction mixture; and (3) the THF solvent in which extensive enolization occurs during reaction of organolithium reagent with a ketone having enolizable hydrogens. In most cases, however, disadvantages 1 and 2 can be circumvented.

Experimental Section

All boiling points and melting points were uncorrected. Infrared spectra were determined with a Beckman IR-33 spectrophotometer. NMR spectra were obtained on a Varian Associates A-60A spectrometer using Me_4Si as the internal standard and deuteriochloroform as the solvent. Concentrations of paramagnetic compounds were measured with the NMR spectrometer according to the method of Evans[22] as it was adapted[23] to the study of equilibra and kinetics of radical ions. Cyclohexane, 20% v/v in carbon tetrachloride, or *tert*-butyl bromide, 50% v/v in carbon tetrachloride, served as external markers. The high-field band of THF served as the internal marker. In the presence of a paramagnetic solute the NMR signals of THF lose their fine structure and are shifted to higher fields. The shift varies linearly with concentration of the paramagnetic solute. A working curve for shift ($\Delta\nu$) vs. lithium benzophenone ketyl concentration was employed. It has the form:

$$\Delta\nu = -6.5 + 79C$$

where $\Delta\nu$ is the position of the high-field band of THF in the solution

Table IV. Boiling or Melting Points of the Alkyl Phenyl Sulfides

Sulfide	Mp or bp (mm), °C	Lit. mp or bp (mm), °C	Ref[a]
$CH_3(CH_2)_6SPh$	85–90 (0.20)	127–129 (2.0)	*b*
$CH_3(CH_2)_7SPh$	120 (0.8)	175 (18)	*c*
$CH_3(CH_2)_3CH(Et)$-CH_2SPh	97–98 (0.05)	160 (12)	*d*
$PhCH_2CH_2SPh$	110–113 (0.15)	188–189 (15)	*e*
$Ph(CH_2)_4SPh$	135–145 (0.20)	153–154 (1.0)	*f*
$PhCH(CH_3)CH_2SPh$	110–115 (0.15)	177–178 (11)	*g*
$Cl(CH_2)_3SPh$	82–84 (0.10)	116–117 (4)	*h*
$Cl(CH_2)_4SPh$	121 (0.20)	155 (12)	*i*
$Cl(CH_2)_5SPh$	101–102 (0.10)	140 (1)	*i*
$Cl(CH_2)_6SPh$	120–122 (0.10)	8	*j*
$PhS(CH_2)_4SPh$	82–83	84.5	*k*
$PhS(CH_2)_6SPh$	76–78	82	*l*

[a] As a general reference see, for example, "Organic Chemistry of Divalent Sulfure", Vol. II, E. E. Reid, Ed., Chemical Publishing Co., New York, N.Y., 1960. [b] K. Takahashi, K. Ohki, T. Mizura, and S. Toyoshima, *Chem. Pharm. Bull. (Tokyo)*, **8**, 757 (1960). [c] H. Burton and N. A. Davy, *J. Chem. Soc.*, 52 (1947). [d] G. Rabilloud, *Bull. Soc. Chim. Fr.*, **2**, 348 (1907). [e] F. Ashworth and G. N. Burkhardt, *J. Chem. Soc.*, 1791 (1928). [f] V. Traynelis and R. F. Love, *J. Org. Chem.*, **26**, 2728 (1961). [g] J. Kenyon, H. Phillips, V. P. Pittmann, R. B. Shakleton, D. E. Kahn, F. H. Yortson, and N. E. Cochinaras, *J. Chem. Soc.*, 1072 (1935). [h] W. R. Kirner and G. H. Richter, *J. Am. Chem. Soc.*, **51**, 3409 (1929). [i] G. M. Bennett, F. Heathcoat, and A. N. Mosses, *J. Chem. Soc.*, 2567 (1929). [j] C. S. Marvel and R. R. Chambers, *J. Am. Chem. Soc.*, **70**, 993 (1948). [k] G. M. Bennett and A. N. Mosses, *J. Chem. Soc.*, 1697 (1931). [l] F. G. Bordwell, H. M. Anderson, and B. M. Pitt, *J. Am. Chem. Soc.*, **76**, 1082 (1954).

of the paramagnetic compound referred to external 20% cyclohexane in CCl_4, in hertz, and C is the concentration of lithium benzophenone ketyl in moles per liter. By subtracting the underlying diamagnetic shift, −6.5 Hz, the shift vs. concentration relation becomes $\Delta\nu = 79C$. In this case $\Delta\nu$ is the *net* paramagnetic shift of the high-field band of THF from any external marker.

The chemicals used in this work were commercial products of Merck-Schuchardt or Fluka, usually 99% pure, and were used without further purification. 4-Phenyl-1-butene was prepared in 64% yield from benzylsodium and allyl bromide following a procedure for preparing *n*-butylbenzene.[24] Allyl benzyl ether was prepared from sodium benzylate and allyl chloride according to the classic Williamson synthesis.

Purification of Tetrahydrofuran. The solvent was stored at least for 1 week over sodium hydroxide pellets, refluxed under nitrogen for several hours over fresh NaOH pellets, and distilled under nitrogen. The distillate was refluxed with sodium metal under nitrogen, distilled once more, and finally redistilled from lithium aluminum hydride containing triphenylmethane indicator under argon. In absolutely anhydrous THF lithium aluminum hydride metalates Ph_3CH rapidly and therefore the final distillation was done after the appearance of the red coloration due to Ph_3CLi.

Preparation of Alkyl Phenyl Sulfides. (A) Photochemical Initiation. An equimolar mixture of the olefin and thiophenol was irradiated with a General Electric 275 W "sunlamp". The progress of the reaction was followed by NMR analysis on aliquots drawn from time to time. No cooling was applied during irradiation, so the temperature of the reaction mixture was usually between 70 and 90 °C.

(B) **Initiation by AIBN.** α,α-Azoisobutyronitrile (50–150 mg) was suspended in part of the olefin and the suspension was added slowly to a stirred and heated (80–90 °C) mixture of thiophenol and the rest of the olefin. The total amount of the olefin was equimolar to thiophenol. Reaction times usually ranged from 2 to 5 h. At the end of the reaction (photochemical or free radical) the mixture was diluted with benzene, the unreacted thiophenol was extracted with sodium hydroxide solution, and finally the product was fractionally distilled after removing benzene. Table IV summarizes the boiling or melting points of the known sulfides and Table V summarizes some data of the sulfides which are new.

Lithium Naphthalene. Lithium naphthalene was prepared by stirring equivalent amounts of naphthalene and lithium chips in THF

Table V. Data of New Sulfides

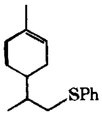
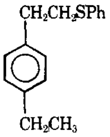
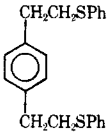
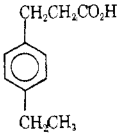
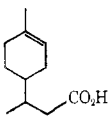
Sulfide	Mp or bp (mm), °C	NMR
$PhO(CH_2)_4SPh$	53	1.76 (m, 4 H, $C(CH_2)C$); 2.86 (t, 2 H, CH_2S); 3.80 (t, 2 H, CH_2O); 7.04 (m, 10 H, two C_6H_5)
$O(CH_2CH_2CH_2SPh)_2$	of high bp	1.84 (m, 4 H, CCH_2C); 2.97 (t, J = 7.5 Hz, 4 H, CH_2S); 3.44 (t, J = 6.1 Hz, 4 H, CH_2O); 7.27 (m, 10 H, two C_6H_5)
	130 (0.15)	1.05 (distorted triplet-like multiplet); 1.73 (br distorted doublet, 14 H); 2.83 (m, 2 H, CH_2S); 5.31 (br s, 1 H, olefinic); 7.20 (m, 5 H, aromatic)
	112–116 (0.05)	1.18 (t, J = 7.8 Hz, 3 H, CH_3); 2.57 (q, 2 H, CH_2CH_3); 2.93 (m, 4 H, CH_2CH_2S); 7.10 (m, 9 H, aromatic)
	of high bp	2.91 (m, 8 H, aliphatic); 7.08 (m, 14 H, aromatic)
$PhS(CH_2)_5SPh$	185–188 (0.03)	1.57 (unsymm t, 6 H, $C(CH_2)_3C$); 2.85 (diffuse t, 4 H, CH_2S); 7.25 (s, 10 H, two C_6H_5)
$PhCH_2O(CH_2)_3SPh$	142–148 (0.10)	1.91 (m, 2 H, CCH_2C); 2.96 (t, J = 7.4 Hz, 2 H, CH_2S); 3.46 (t, J = 6.0 Hz, 2 H, CH_2O); 4.38 (s, 2 H, CH_2Ph); 7.18 (s, 10 H, two Ph)
$(CH_3)_3CCH_2CH_2SPh$	72–74 (0.05)	0.91 (s, 9 H, $(CH_3)_3C$); 1.54 (m, 2 H, CH_2Bu-*t*); 2.85 (m, 2 H, (CH_2S); 7.17 (s, 5 H, aromatic)
$PhCH_2CH_2CH_2SPh$	125–130 (0.20)	1.94 (m, 2 H, CCH_2C); 2.76 (q, 4 H, CH_2Ph, CH_2S); 7.17 (d, 10 H, two C_6H_5)
$PhCH_2O(CH_2)_4SPh$	155 (0.03)	1.70 (m, 4 H, $C(CH_2)_2C$); 2.87 (diffuse t, 2 H, CH_2S); 3.43 (diffuse t, 2 H, CH_2O); 4.42 (s, 2 H, CH_2Ph); 7.25 (s, 10 H, two C_6H_5)
$Ph_2CHCH_2CH_2SPh$	69–71	2.37 (t, $J \simeq$ 7.8 Hz, 2 H, CCH_2C); 2.81 (distorted t, 2 H, CH_2S); 4.09 (t, $J \simeq$ 7.8 Hz, 1 H, CHPh); 7.17 (s, 15 H, three C_6H_5)
$Ph_3CCH_2CH_2SPh$	117–119	2.78 (q, 4 H, aliphatic); 7.17 (s, 20 H, four C_6H_5)
Ph_2CHCH_2SPh	44–46	3.56 (unsym d, J = 7.6 Hz, 2 H, (CH_2S); 4.20 (unsym t, 1 H, (CHPh); 7.20 (s, 15 H, three C_6H_5)

Table VI. Data of New Carboxylic Acids

Carboxylic acid	Registry no.	Mp or bp (mm), °C	NMR
n-BuCH(Et)CH_2CO_2H	14272-47-0	83.5 (0.25)	0.89 (distorted t), 1.29 (m) and 1.92 (br t, 15 H); 2.20 (s, 1 H, $HCHCO_2$); 2.30 (singlet-like d, $J \simeq 1$ Hz, 1 H, $HCHCO_2$); 11.25 (s, 1 H, acidic)
$PhCH(CH_3)CH_2CO_2H$	4593-90-2	94 (0.15)	1.28 (d, $J = 7.0$ Hz, 3 H, CH_3); 2.46 (d, $J \simeq 2$ Hz, 1 H, $HCHCO_2$); 2.59 (s, 1 H, $HCHCO_2$); 3.19 (m, 1 H, CHPh); 7.12 (s, 5 H, arom); 11.35 (s, 1 H, acidic)
	64740-36-9	106-108 (0.15)	1.20 (t, $J = 7.8$ Hz, 3 H, CH_3); 2.65 (m, 6 H, CH_2CH_2 + CH_2CH_3); 7.00 (d, 4 H, arom); 11.45 (s, 1 H, acidic)
$PhS(CH_2)_6CO_2H$	64740-37-0	63-65	1.00-1.90 (br band, 8 H, $C(CH_2)_4C$); 2.23 (unsym t, 2 H, CH_2CO_2); 2.78 (unsym t, 2 H, CH_2S), 7.11 br s, 5 H, arom); 10.6 (s, 1 H, acidic)
	64740-38-1	115-116 (0.20)	1.00 (d); 1.00-2.50 (br unsym d); 2.33 (q, 16 H); 5.31 (br s, 1 H, olefinic); 11.35 (s, 1 H, acidic)
$PhCH_2O(CH_2)_4CO_2H$	64740-39-2	Viscous liquid	1.62 (br s, 4 H, $C(CH_2)_2C$); 2.26 (diffuse t, 2 H, CH_2CO_2); 3.37 diffuse t, 2 H CH_2O), 4.40 (s, 2 H, CH_2Ph); 7.20 (s, 5 H, arom); 11.30 (s, 1 H, acidic)

under argon in a concentration of 1.0 M. Under these conditions the complete dissolution of the metal requires stirring for 6 h or longer, depending on the efficiency of the stirrer. A glass-coated stirring bar should be employed, because lithium naphthalene reacts with Teflon. The total alkalinity in a hydrolyzed aliquot of lithium naphthalene solution can be taken as the concentration of $Li^+C_{10}H_8^{-\cdot}$, provided the THF used is absolute. This has been checked by double titration using ethylene bromide.

Examplary Runs. (a) With Lithium Naphthalene. (i) Normal Addition. 2-Ethylhexyllithium. The reaction system was a three-neck 100-mL flask equipped with a glass-coated stirring bar and a low-temperature thermometer and connected through the central neck to a vacuum–argon line. The third side neck was stoppered with a rubber septum. The air inside the reaction flask was replaced by pure argon and 20 mL of 1.0 M lithium naphthalene solution was transferred in the flask with a syringe lubricated with silicon oil. The flask was immersed into a dry ice–acetone bath and 2.25 g (10 mmol) of 2-ethylhexyl phenyl sulfide was added with a syringe to the stirred lithium naphthalene at −55 to −45 °C. The resulting mixture was stirred for about 2 min at −50 °C and then the temperature was allowed to rise to −20 °C in order to ensure completion of the reaction. At this stage the color of the mixture was brownish red. The temperature was brought down to −60 °C and the mixture was carbonated with a slurry of crushed solid carbon dioxide in diethyl ether. The carbonation mixture was allowed to attain room temperature, water (50 mL) was added, and the volume of the mixture was reduced in a rotary evaporator. Sodium hydroxide pellets (~2 g) and 1 mL of 30% hydrogen peroxide were added to the carbonation mixture. After stirring for about 0.5 h naphthalene and other neutral products were extracted with 100 mL of benzene, the water layer was extracted once more with 100 mL of hexane, and then it was acidified with 20% sulfuric acid. The liberated carboxylic acid was extracted with 3 × 100 mL of ether, the ether extracts were dried over anhydrous magnesium sulfate for at least 12 h, and after removing the drying agent the ether was distilled to leave 1.33 g (84%) of a liquid acid whose NMR spectrum agreed with the expected structure, n-BuCH(Et)CH_2CO_2H.

(ii) Inverse Addition. 3-Thiophenoxypropyllithium. 3-Chloropropyl phenyl sulfide (4.7 g, 25 mmol) was diluted with 20 mL of anhydrous THF and placed in a 250-mL three-necked flask equipped with a glass-coated stirring bar, a pressure-equalizing addition funnel, and low-temperature thermometer and connected to a vacuum–argon line. Under an atmosphere of argon, 50 mL of 1.0 M $Li^+C_{10}H_8^{-\cdot}$ was transferred in the addition funnel, and the solution was added dropwise at −60 ± 5 °C during a period of about 0.5 h. After the addition the mixture was stirred for 0.25 h between −60 and −70 °C and the reaction became complete by allowing the temperature to rise to −40 °C. The mixture was carbonated as usual and the carbonation mixture was worked up as described in the previous paragraph, avoiding only the treatment with hydrogen peroxide. Acidifcation of the water layer afforded 2.6 g of solid acid and an additional 0.3 g by ether extraction of the filtrate, yielding 2.9 g (59% of theory) of $PhSCH_2CH_2CH_2CO_2H$, which melted at 64–66 °C after one recrystallization from hexane (lit.[25] mp 69–71 °C).

(B) With Lithium Dispersion. 1,7-Dilithio(4-oxaheptane). The reaction system was a 1-L, three-neck flask equipped with a Hershberg stirrer made of Nichrome wire and having a ST 30 ball-joint seal, a thermometer, and a reflux condenser. The stirrer was driven by a ⅛ hp motor operating at 3000 rpm maximum speed (Voss Instruments LTD Maldon, Essex, England). The upper end of the condenser was connected to a system permitting the evacuation of the flask, the filling up of the reaction system with argon, and the maintainance of a small positive pressure of argon during operation. Lithium metal dispersion, prepared in situ from 1.8 g of lithium metal, 100 mL of mineral oil, and 0.3 g of palmitic acid stabilizer, was freed from mineral oil by washing with dry benzene. THF (130 mL) and 1.0 g of naphthalene were added to the reaction and the resulting mixture was stirred while the temperature was brought to −40 °C. 3,3′-Bis(thiophenoxypropyl) ether (15 g, 47 mmol) was added at once. Stirring was continued for 2.5 h, vigorously, while the temperature was kept below −20 °C. The mixture was carbonated by pouring it rapidly into a large beaker containing crushed dry ice and anhydrous ether. When the mixture of carbonation came to room temperature, water (200 mL) was added, followed by 5 g of sodium hydroxide pellets and 13 mL of dimethyl sulfate. After stirring for about 1 h the mixture was evaporated to smaller volume in a rotary evaporator. Thioanisole and other neutral products were removed by washing the water layer with hexane. Acidification with 20% sulfuric acid caused the precipitation of a solid acid which was isolated by ether extraction (3 × 100 mL). The dry product of $O(CH_2CH_2CH_2CO_2H)_2$ weighed 7.61 g, or 90% of theory, and melted at 78–80 °C after one recrystallization from hexane (lit.[26] mp 81 °C).

Table VI summarizes some data of carboxylic acids which have not been reported before.

4-Chlorobutyl Phenyl Sulfide. A mixture of 1,4-dichlorobutane (101.5 g), thiophenol (52 mL, 0.5 mol), water (150 mL), and sodium hydroxide (25 g) was stirred magnetically and refluxed for 2 h. The products and excess dichlorobutane were taken up in benzene (150 mL) and the benzene solution was dried over anhydrous $MgSO_4$ and evaporated to smaller volume in a rotary evaporator. Vacuum distillation gave 64.4 g of 4-chlorobutyl phenyl sulfide (65%), bp 103 °C (0.05 mm), and a residue in the distillation flask (~13 g) which was 1,4-dithiophenoxybutane, mp 82 °C (from methanol) (lit.[27] mp 84 °C).

4-Phenoxybutyl Phenyl Sulfide. Following a procedure for making *sec*-butyl phenyl ether,[28] a solution of 20 g of phenol and 20.05 g (0.1 mol) of 4-chlorobutyl phenyl sulfide in 50 mL of diethylene glycol was heated and stirred in the presence of 15 g of anhydrous potassium carbonate for 1.5 h at 125–135 °C. The mixture was poured into a beaker containing 250 mL of water. A solid product precipitated which was separated and dissolved in 100 mL of benzene, and the benzene solution was washed with sodium hydroxide solution, then with water and finally dried over anhydrous $MgSO_4$. Evaporation of benzene left 24.0 g (93%) of crystalline product. Recrystallization from ethanol gave shiny flakes, mp 53 °C.

4-Benzyloxybutyl Phenyl Sulfide. Sodium metal (8.0 g) was dissolved in 70 mL of benzyl alcohol, 80 mL of anhydrous THF, and 20 mL of dry benzene by stirring at the reflux temperature for several hours under argon. To this mixture was added 58 g of 4-chlorobutyl phenyl sulfide at once and the resulting mixture was stirred at reflux for 17 h. Water (100 mL) was added followed by benzene (250 mL) and the mixture was stirred for a few minutes, the organic layer was separated, dried over anhydrous $MgSO_4$, and finally concentrated to a smaller volume in a rotary evaporator. Vacuum distillation afforded a fraction boiling (0.05 mm) at 155–160 °C, which weighed 42.5 g (53%), and it was (NMR) 4-benzyloxybutyl phenyl sulfide.

Disulfides $PhS(CH_2)_nSPh$ (n = 2–6). They were prepared from the corresponding dichlorides or dibromides and an excess of thiophenol by refluxing with aqueous sodium hydroxide for 3 h. The yields are given in Table II.

3,3,3-Triphenylpropyl Phenyl Sulfide. This sulfide was prepared by coupling tritryllithium with 2-bromoethyl phenyl sulfide[29] ($BrCH_2CH_2SPh$). To a mixture of triphenylmethane (12.2 g, 50 mmol) and 20 mL of dry benzene under argon was added butyllithium (50 mL, 1.54 M in benzene) followed by 40 mL of absolute THF at 0–10 °C. The resulting mixture was stirred for 24 h at room temperature in order to ensure the complete destruction of the excess butyllithium by THF cleavage. 2-Bromoethyl phenyl sulfide (10.85 g, 50 mmol) was dissolved in 20 mL of dry benzene and added to the trityllithium solution at 10–35 °C. After stirring for 2 h, the mixture was hydrolyzed and diluted with benzene, and the organic layer was separated, washed with water, and dried over anhydrous $MgSO_4$. Evaporation of benzene in the rotary evaporator left a pale yellow crystalline mass. This material was washed with hot methanol, then recrystallized from hexane to afford 15.4 g (81%) of white crystals, mp 117–119 °C. The NMR spectrum of this compound agreed with the structure of the title compound.

Reaction of 3,3,3-Triphenylpropyl Phenyl Sulfide with Lithium Naphthalene. To 50 mL of 1.0 M lithium naphthalene was added a solution of 9.3 g (25 mmol) of 3,3,3-triphenylpropyl phenyl sulfide in 40 mL of absolute THF at −55 to −50 °C. The red reaction mixture was carbonated as usual. During workup of the carbonation mixture a crystalline precipitate formed from the aqueous layer, which was isolated by filtration. The precipitate was washed with water followed by benzene and air dried. Acidification of the water layer afforded a small amount of acidic product. Both melted at 262–268 °C and the combined yield was 3.92 g (or 54%) of triphenylacetic acid (lit.[30] mp 264–265 °C).

Trapping of Ethylene, Evolved during Reaction of 3,3-Diphenylpropyl Phenyl Sulfide with Lithium Naphthalene, by Cyclohexyllithium.[31] To 50 mL of 1.0 M lithium naphthalene in THF was added chlorocyclohexane (1.7 g, ~14 mmol) dissolved in 10 mL of THF at −40 to −50 °C. Immediately after the addition of the chloride, a solution of 3.75 g (12.5 mmol) of 3,3-diphenylpropyl phenyl sulfide in 15 mL of THF was introduced into the reaction system containing the mixture of cyclohexyllithium and lithium naphthalene at −55 to −50 °C. The resulting mixture was stirred while the temperature was allowed to rise gradually to −10 °C during a period of about 1 h. Carbonation afforded 3.7 g of acidic products, partially crystalline: NMR ($CDCl_3$) 2.32 (distinct triplet, protons α to the carboxyl group[19a] of 3-cyclohexylpropionic acid), ~5.04 ppm (singlet, methinic protons of diphenylacetic acid), along with resonances in the aromatic and aliphatic regions. In a separate experiment 3,3-diphenylpropyl phenyl sulfide was cleaved by lithium naphthalene in the absence of trapping agent. In this case an 88% yield of diphenylacetic acid was isolated after carbonation.

1,1,3-Triphenylbutanol. To a solution of 2-phenylpropyllithium, prepared from 25 mmol of 2-phenylpropyl phenyl sulfide, was added a solution of 4.6 g (25 mmol) of benzophenone in 10 mL of THF at −10 to +20 °C. The resulting blue solution was tested for paramagnetism and it was paramagnetic. A net paramagnetic shift of 4.5 ± 0.5 Hz was measured which corresponds to a benzophenone concentration of 0.057 M. The total volume of the reaction mixture was 65 mL. Thus the total amount of lithium benzophenone ketyl was 65 × 0.057 = 3.7 mmol, or 14.8% based on the benzophenone used. The reaction mixture after stirring for 2 h at room temperature was subjected to steam distillation. The nonvolatile product was extracted with benzene, and the benzene layer was washed with sodium hydroxide solution, then with water, and finally dried over $MgSO_4$. Evaporation of benzene in a rotary evaporator to constant weight left 6.9 g of crude product from which by recrystallization from hexane 5.1 g (68%) of 1,1,3-triphenylbutanol was isolated, mp 90–92 °C, after two recrystallizations from hexane.

1,1-Diphenyl-5-phenylthiohexanol. This carbinol was prepared in a 25 mmol run from benzophenone and 5-thiophenoxypentyllithium. The latter was prepared from 5-chloropentyl phenyl sulfide according to the procedure for preparing 3-thiophenoxypropyllithium. The crude product, which weighed 6.9 g, was applied to a column of 100 g of neutral alumina. Elution with benzene afforded unreacted sulfide. Further elution with ether–benzene (30:70 v/v %) yielded benzophenone. Elution with chloroform gave 2.9 g (33%) of the title carbinol (NMR data in Table III).

1-(2-Phenylpropyl)cyclohexanol. To a solution of 2-phenylpropyllithium, prepared from 25 mmol of 2-phenylpropyl phenyl sulfide, was added 3.5 mL of cyclohexanone at −20 to 0 °C. The mixture was stirred for about 0.25 h and subjected to steam distillation. The nonvolatile product was extracted with benzene and the benzene solution was dried over anhydrous $MgSO_4$ and evaporated to constant weight. The product, a liquid, weighed 3.0 g. A portion of this material (2.35 g) was chromatographed on 100 g of neutral alumina. Elution with benzene yielded unreacted sulfide. Further elution with ethanol–chloroform (30:70 v/v %) afforded 1.20 g (28%) of a liquid whose NMR spectrum (see Table III) agreed with the title compound.

Reaction of $PhS(CH_2)_6SPh$ with 4 Equiv of Lithium Naphthalene. A solution of 3.78 g (12.5 mmol) of 1,6-dithiophenoxyhexane in 25 mL of THF was added to 50 mL of 1.0 M lithium naphthalene at −40 to −30 °C. The resulting mixture was stirred at −60 °C for about 0.25 h and then the temperature was allowed to rise to −30 °C in order to bring the reaction to completion. The mixture was cooled down to −70 °C and carbonated. From the carbonation mixture, after oxidation of thiophenol with alkaline H_2O_2, an acid product was isolated as usual. The acidic product weighed 3.70 g and exhibited an NMR spectrum with resonances in the aromatic region, a broad doublet-like multiplet extending from 6.90–7.65 ppm, a band at 6.1 ppm, dihydronaphthalene derivatives(s) as well as resonances in the aliphatic region. Repeated recrystallizations of the crude product from hexane afforded 0.6 g of 1,8-octanedioic (suberic) acid, mp 135–140 °C (lit.[32] 140–144 °C). Similarly, the disulfides $PhS(CH_2)_nSPh$ (n = 4, 5) upon reaction with 4 equiv of lithium naphthalene and subsequent carbonation afforded acidic products, the weights of which exceeded considerably the corresponding theoretical yields, calculated as $(CH_2)_n(CO_2H)_2$. Their NMR spectra also indicated that they were derivatives of naphthalene.

Registry No.—Lithium naphthalene, 7308-67-0; lithium, 7439-93-2.

References and Notes

(1) B. J. Wakefield, "The Chemistry of Organolithium Compounds", Pergamon Press, Oxford, 1974, p 21; G. E. Coates, M. L. H. Green, and K. Wade, "Organometallic Compounds", Vol. I, Mathuen and Co., Ltd., London, 1969, p 6.

(2) For an excellent discussion of heteroatom–carbon bond cleavage with pertinence to organometallic chemistry, see J. J. Eisch, "The Chemistry of Organometallic Compounds, the Main Group Elements", Macmillan, New York, N.Y., 1967, p 13.

(3) (a) N. L. Holy, *Chem. Rev.*, **74,** 243 (1974); (b) H. Gilman and H. A. McNinch, *J. Org. Chem.*, **26,** 3723 (1961).

(4) J. J. Eisch and A. M. Jacobs, *J. Org. Chem.*, **28,** 2145 (1963).

(5) C. G. Screttas and M. Micha-Screttas, Abstracts, 7th International Conference on Organometallic Chemistry, Venice, Italy, Sept 1–5, 1975, paper no. 56.

(6) M. W. Hanna, *J. Chem. Phys.*, **37,** 685 (1962); K. Issleib and H. O. Fröhlich, *Z. Naturforsch. B.*, **14,** 349 (1959).

(7) The involvement of carbanions in the reaction of aromatic radical anions with substrates containing carbon–heteroatom bonds, such as alkyl halides, has been established mainly by the work of J. F. Garst [J. F. Garst, P. W. Ayers, and R. C. Lamb, *J. Am. Chem. Soc.*, **88,** 4260 (1966); J. F. Garst, *Acc. Chem. Res.*, **4,** 400 (1971); J. F. Garst in "Free Radicals", J. K. Kochi, Ed., Wiley, New York, N.Y., 1973, p 503] and by the work of others [S. J. Cristol and R. V. Barbour, *J. Am. Chem. Soc.*, **88,** 4262 (1966); G. D. Sargent, J. N. Cron, and S. Bank, *ibid.*, **88,** 5363 (1966)].

(8) M. Schlosser, *Newer Methods Prep. Org. Chem.*, **5,** 301 (1968).

(9) C. G. Screttas, *J. Chem. Soc., Chem. Commun.*, 869 (1972).

(10) The pseudohalogen behavior of the group PhS– is also indicated by its ability to undergo a reaction analogous to halogen–metal interconversion: D. Seebach, *Chem. Ber.*, **105,** 487 (1972).

(11) M. S. Kharasch and F. R. Mayo, *J. Am. Chem. Soc.*, **55,** 2468 (1933).

(12) S. C. Honeycutt, *J. Organomet. Chem.*, **29,** 1 (1971); R. B. Bates, L. M. 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).

(13) This statement is based on the rapidity with which a sulfide reacts with lithium naphthalene, rather than on the yield of the produced alkyllithium.

(14) This could be true for up to a certain limit of electron affinity of the substrate.

Usually, very high electron affinity is accompanied by great stability of the radical anion produced by electron acceptance. In such a case the fission of the radical anion becomes rate determining.

(15) (a) K. Higashi, H. Baba, and A. Rembaum, "Quantum Organic Chemistry", Interscience, New York, N.Y., 1965, p 312. (b) The pK_a value of benzyl phenyl sulfide, for example, is 30.8: F. G. Bordwell, J. E. Bares, J. E. Bartmess, G. E. Drucker, J. Gerhold, G. J. McCollum, M. Van Der Puy, N. R. Vanier, and W. S. Matthews, *J. Org. Chem.*, **42**, 326 (1977). For its metalation see: J. F. Biellmann and J. B. Ducep, *Tetrahedron Lett.*, 5629 (1968).

(16) (a) The pK_a values of HCl, PhOH, and PhSH were taken from "Lange's Handbook of Chemistry", J. A. Dean, Ed., McGraw-Hill, New York, N.Y., 1973, section 5. (b) The pK_a of Ph_2PH was quoted by A. Tzschach, Abstracts of Papers, 1st European Conference on Organometallic Chemistry (Main Group), Warsaw, Poland, Sept 21–24, 1976, No. II.3.6.

(17) C. D. Hurd and K. Wilkinson, *J. Am. Chem. Soc.*, **71**, 3429 (1949).

(18) C. D. Wooster and R. A. Morse, *J. Am. Chem. Soc.*, **56**, 1735 (1934). Pertinent is also the fragmentation of 3,3,3-triphenylpropyl iodide during halogen-metal exchange with butyllithium in THF at −40 °C: H. P. Fischer, E. Kaplan, and P. Neuenschwander, *Chimia*, **22**, 338 (1968).

(19) (a) P. D. Bartlett, S. J. Tauber, and W. P. Weber, *J. Am. Chem. Soc.*, **91**, 6362 (1969): (b) L. Spialter and C. W. Harris, *J. Org. Chem.*, **31**, 4263 (1966).

(20) A. L. J. Beckwith *Org. Chem., Ser. One*, **10**, W. A. Waters, Ed., Butterworths, London, University Park Press, Baltimore, Md., 1973, p 28.

(21) According to a suggestion made by a referee, these fragmentations are pertinent to the fission of diarylethane radical anions to arylmethyl carbanions, e.g., A. Lagendijk and M. Szwarc, *J. Am. Chem. Soc.*, **93**, 5359 (1971), as both involving C–C bond cleavage. However, in the case of these sulfides the bond which undergoes fission is a C–S bond, followed by fragmentations which leads to a C–C bond cleavage indirectly. The direct C–C fission is a considerably slower process than any of these fragmentations. The Fragmentation reaction was complete on contact of the sulfide with the lithium naphthalene, whereas the direct C–C fission appears to have half-lives of the order of several minutes or longer.

(22) D. F. Evans, *Proc. Chem. Soc.*, 115 (1958); *J. Chem. Soc.*, 2003 (1959).

(23) C. G. Screttas, *J. Chem. Soc., Chem. Commun.*, 869 (1972); *J. Chem. Soc., Perkin Trans. 2*, 745 (1974); C. G. Screttas and D. G. Georgiou, *Tetrahedron Lett.*, 417 (1975).

(24) M. Schlösser, *Newer Methods Prep. Org. Chem.*, **5**, 303 (1968).

(25) G. Kresse, W. Schramm, and G. Cleve, *Chem. Ber.*, **94**, 2060 (1961).

(26) T. Haga, *Nippon Kagaku Zasshi*, **81**, 1113 (1960); *Chem. Abstr.*, **56**, 5827g (1961).

(27) Footnote *k*, Table IV.

(28) M. Micha-Screttas and C. G. Screttas, *J. Org. Chem.*, **42**, 1462 (1977).

(29) E. D. Amstutz, *J. Org. Chem.*, **9**, 310 (1944).

(30) Reference 16a, section 7-384.

(31) C. G. Screttas, *J. Chem. Soc., Chem. Commun.*, 752 (1972).

(32) Reference 16a, section 7-350.

Halogenated Carbonyl Ylides in the Reactions of Mercurial Dihalocarbene Precursors with Substituted Benzaldehydes

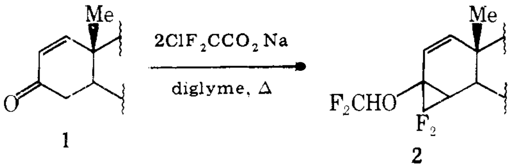
Charles W. Martin, Paul R. Lund, Erich Rapp, and John A. Landgrebe*

Department of Chemistry, University of Kansas, Lawrence, Kansas 66045

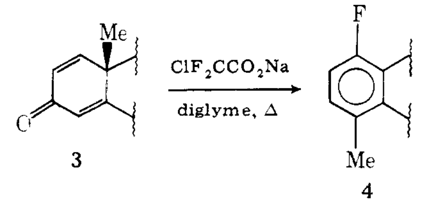
Received January 3, 1977

The reactions of phenyl(bromodichloromethyl)mercury (12) with several aromatic aldehydes (benzene, 80 °C; followed by treatment with methanol and pyridine at 0 °C) were investigated: [aldehyde (significant products)] **11a** (CO, **13a**, **14a**); **11b** (CO, **13b**, **14b**); **11c** (CO, **14c**, **15c**, **16c**); **11d** (CO, **14d**). Relative reactivities with respect to mercurial **12** (benzene, 80 °C) were 3-CF_3PhCHO (0.08), PhCHO (0.3), *n*-$BuCH{=}CH_2$ (0.3), 4-MeOPhCHO (0.9), c-C_6H_{10} (1.0), and $Me_2C{=}CMe_2$ (15.0). Complexation between the mercurial and benzaldehyde, which enhanced the rate of decomposition of the mercurial to produce $:CCl_2$ of the same reactivity as that from the mercurial alone, was observed. Evidence suggests the intermediacy of dichlorocarbonyl ylides.

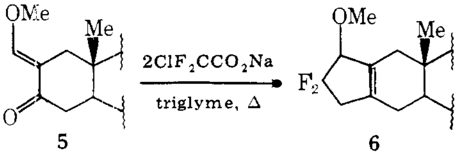
Despite the availability of dihalocarbene precursors (which upon decomposition do not first produce the trihalomethyl anion), there are few examples of the reactions of such divalent intermediates with simple aldehydes and ketones.[1] Difluorocarbene from the apparently concerted decomposition of sodium chlorodifluoroacetate[3] reacts with steroidal enones such as **1** to produce, among other products, bis(difluorocarbene) adduct **2**,[4] with steroidal dienone **3** to form a small yield of rearranged aromatic fluoride **4**,[4c] and with methoxymethylene keto steroid **5** to form the product of a net 1,4 addition.[5]



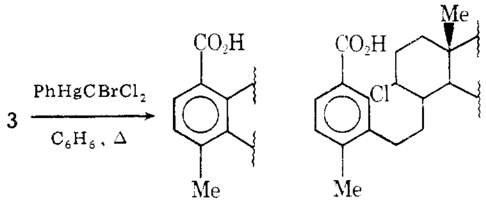
1 2



3 4

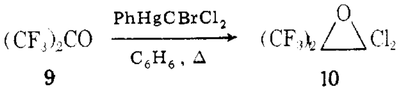


5 6



7 8

The attack of phenyl(bromodichloromethyl)mercury (with presumed intervention of dichlorocarbene)[6] on ketone **3** produced rearranged structures **7** and **8**.[7] Seyferth[8] has found that the attack of the same mercurial on highly halogenated aldehydes and ketones frequently produced isolable dichlorooxiranes. Merz[2d] has shown that dichlorocarbene can be used to convert aromatic aldehydes to the corresponding mandelic acids.



9 10

In preliminary communications[9,10] we have noted a variety of interesting and previously unobserved products from the reaction of phenyl(bromodichloromethyl)mercury (**12**) with benzaldehyde and benzophenone. We now report in more detail on the reactions of the mercurial with a series of substituted benzaldehydes.

Results and Discussion

Mercurial Decomposition. Although the addition of an equimolar amount of phenyl(bromodichloromethyl)mercury

0022-3263/78/1943-1071$01.00/0