8.00 mmol), and W(CO)$_6$ (2.81 g, 8.00 mmol) in DME (40 ml) was heated to 90° for 48 hr. Work-up as described for the reaction of the same α-chloro ketone with Mo(CO)$_6$ gave 3, R = pentamethylphenyl, in 2% yield, along with recovered starting materials. Using a reaction time of 6 days resulted in the formation of methyl ketone in 12% yield.

Reaction of 2-Chloro-2′,3′,4′,5′,6′-pentamethylacetophenone with Triphenylphosphine Molybdenum Pentacarbonyl. A DME (60 ml) solution of (C$_6$H$_5$)$_3$PMo(CO)$_5$ (2.611 g, 5.20 mmol) and α-chloro ketone (1.17 g, 5.20 mmol) was heated at 85–90° for 46 hr. The solution was cooled and filtered into ice–water. The resulting precipitate was filtered and dried. Continuous extraction of the solid with petroleum ether gave reasonably pure methyl ketone [(C$_6$H$_5$)$_3$PMo(CO)$_5$ as impurity] which could be furthur purified by column chromatography on Florisil using petroleum ether as eluent. No α,β-unsaturated carbonyl was obtained by treatment of the nonextractable material with ether–chloroform.

Reaction of 2-Bromo-4′-phenylacetophenone with Tetrabutylammonium Pentacarbonyl Molybdenate(0). A mixture of tetrabutylammonium pentacarbonyl molybdenate(0)[6] (0.918 g, 2.10 mmol) and 2-bromo-4′-phenylacetophenone (0.578 g, 2.10 mmol) in DME (45 ml) was heated at 90° for 48 hr. The reaction mixture was worked up as described in procedure A to give 3 and 5, R = p-C$_6$H$_5$C$_6$H$_4$.

Reaction of Dichlorodiphenylmethane (7) with Mo(CO)$_6$. A mixture of dichlorodiphenylmethane (1.90 g, 8.00 mmol) and Mo(CO)$_6$ (4.20 g, 16.0 mmol) in dry DME (40 ml) was heated at 85–90° for 48 hr. The solution was cooled and poured into cold water. The resulting solid was filtered to give crude tetraphenylethylene (8). Chromatography of the latter on silica gel, using benzene as eluent, gave 0.864 g (65%) of pure 8: mp 223.5–225.0° (lit.[1] mp 226–227°); mass spectrum m/e 332 (M$^+$).

Reaction of 1,2-Dichloro-1,1,2,2-tetraphenylethane with

Mo(CO)$_6$. A mixture of 1,2-dichloro-1,1,2,2-tetraphenylethane (2.02 g, 5.00 mmol) and Mo(CO)$_6$ (2.37 g, 9.00 mmol) in DME (40 ml) was heated at 85–90° for 42. hr. Work-up as described for 7 gave tetraphenylethylene in 81% yield.

Reaction of 9-Bromofluorene with Mo(CO)$_6$. A solution of 9-bromofluorene (2.14 g, 8.60 mmol) and Mo(CO)$_6$ (2.29 g, 8.65 mmol) in DME (30 ml) was heated at 90–95° for 45 hr. The solution was cooled and filtered (inorganic) into ice water to give a white solid which was subsequently filtered. Recrystallization from benzene–ethanol gave 0.580 g (40%) of bisfluorenyl (10), mp 246–248° (lit.[7] mp 246°). Spectral data for 10 were in accord with data for authentic material.

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Kinetics of the Reaction of n-Butyllithium
with 4-Methylmercaptoacetophenone in Benzene[1]

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Kinetics of the reaction of 4-methylmercaptoacetophenone (2) with excess n-butyllithium in benzene at 25.0 °C have been studied by ir and uv stopped-flow spectrophotometric techniques. The observed first-order rate constant increases rapidly as the concentration of n-butyllithium is increased from 0.014 to ca. 0.1 M, but the rate is not greatly enhanced by further increases in the concentration of alkyllithium. The rate of the reaction is increased by the presence of alkoxides in the alkyllithium reagent; addition of 0.001 M of the product alcohol to 0.1 M n-butyllithium increases the measured first-order rate constant by a factor of about 2. Some mechanistic implications of these observations are outlined.

The reaction of the ketone 2,4-dimethyl-4′-methylmercaptobenzophenone (1) with methyllithium in diethyl ether has been shown[2] to be first order in ketone and one-fourth order in methyllithium. These data are consistent with a mechanism for addition proceeding through monomer in equilibrium with tetrameric methyllithium. Other examples of reactions occurring through monomeric organolithium, which is in equilibrium with higher aggregates in ethereal solvents, include the addition of n-butyllithium[3] and phenyllithium[3] to benzonitrile, the addition of methyllithium to transition metal carbonyls,[4] the initiation of vinyl polymerization,[5,6] and the metalation of triphenylmethane.[7] The addition of alkyllithium reagents to styrene[8–10] and to 1,1-diphenylethylene[11,12] in aromatic solvents is also believed to proceed through monomeric species; however, for the addition of n-butyllithium to butadiene[13] and ethyllithium to 1,1-diphenylethylene[14] in aromatic solvents, monomer may not be the sole reactive species. In aliphatic solvents, alkyllithium reagent aggregates species appear to react with isoprene[15–17] and ethylene.[18]

The addition of lithium halides to diethyl ether solutions of methyllithium has been shown[2] to retard the rate of addition to ketone 1. This is the expected result because the incorporation of lithium halides into methyllithium aggregates lowers the fraction of the organolithium present in monomeric form.[2]

In contrast to the rate-depressing effect of lithium halides in diethyl ether on the addition to ketones, alkoxides have been reported to either increase or decrease the reactivity of alkyllithium reagents in hydrocarbons. For example, the initiation of styrene polymerization in aromatic solvents,[19–21] the propagation of olefin polymerizations,[15,16,19,21,22] and the alkylation of naphthalene[23] are depressed by lithium alkoxides, while in contrast alkoxides
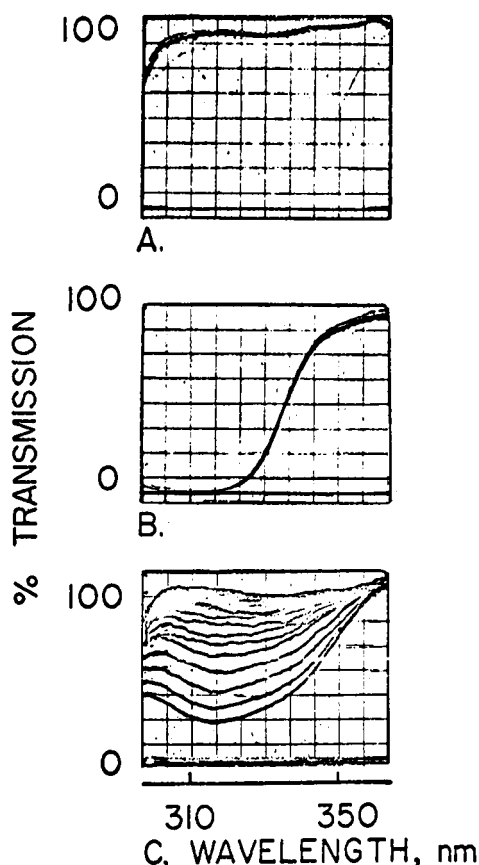
Figure 1. Transmission spectra of the reaction of 8 × 10⁻³ M n-butyllithium with 6.1 × 10⁻⁵ M 2,4-dimethyl-4'-methylmercaptobenzophenone in benzene at 25.0 °C: A, transmission spectrum of 8 × 10⁻³ M n-butyllithium in benzene; B, transmission spectrum of 6.1 × 10⁻⁵ M 2,4-dimethyl-4'-methylmercaptobenzophenone in benzene; C, transmission spectrum of the reaction mixture of 8 × 10⁻³ M n-butyllithium and 6.1 × 10⁻⁵ M 2,4-dimethyl-4'-methylmercaptobenzophenone in benzene at 25.0 °C, recorded 18.2 times per second. The first recorded line is the continuous flow spectrum, recorded at 0.03 s after mixing.

accelerated the rate of the initiation of olefin polymerization in aliphatic solvents,[15-17] the addition of ethyllithium[14] and n-butyllithium[24] to 1,1-diphenylethylene in benzene, the pyrolysis of sec-butyllithium[25] in octane and tert-butyllithium[26] in decalin, and the cleavage of n-butyl and tert-butyl ethers by n-butyllithium in heptane.[27,28]

In the present study, the kinetics of the reaction of n-butyllithium with 4-methylmercaptoacetophenone (2) in benzene are examined, eq 1. Reacting solutions were ob-

$$(n\text{-Bu})_6\text{Li}_6 \ + \ CH_3S\text{—}\langle\bigcirc\rangle\text{—}\overset{\overset{\displaystyle O}{\|}}{C}CH_3 \ \xrightarrow[25°]{C_6H_6} \ \xrightarrow{H_3O^+}$$

$$CH_3S\text{—}\langle\bigcirc\rangle\text{—}\underset{\underset{\displaystyle CH_2CH_2CH_2CH_3}{|}}{\overset{\overset{\displaystyle OH}{|}}{C}}\text{—}CH_3 \qquad (1)$$
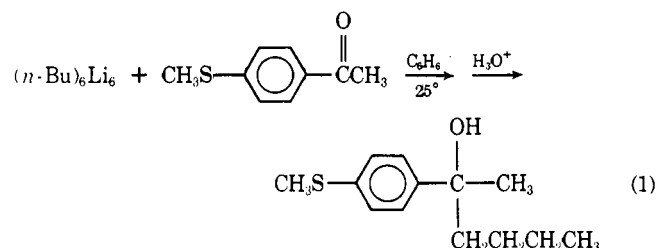
served by ir and uv stopped flow spectrophotometric techniques. The effect of added alkoxides is also considered.

Results and Discussion

The continuous flow uv spectrum of the reaction mixture of n-butyllithium and 4-methylmercaptoacetophenone (2) in benzene at 25.0 °C, recorded ca. 1 ms after mixing, indicates that the π–π* absorption of ketone 1 is broadened, compared to the spectrum of ketone in the absence of n-

Table I. Reaction of 0.13 M n-Butyllithium with 1.3 × 10⁻³ M 4-Methylmercaptoacetophenone in Benzene at 25.0° C

Time, s	Absorbance at 330 nm	k_{obsd}, s⁻¹ (integrated)
0.0	0.917	
0.01	0.602	42
0.02	0.394	42
0.03	0.255	43
0.04	0.159	44
0.05	0.093	46
0.06	0.056	47
0.07	0.040	45
0.08	0.022	47
	Least-squares rate constant	46.7

Table II. Effect of Ketone Concentration on the Observed First-Order Rate Constant for the Reaction of 0.19 M n-Butyllithium with 4-Methylmercaptoacetophenone (1) in Benzene at 25.0°C

10³ ketone 1, M	k_{obsd}, s⁻¹
0.125	115
0.25	91
0.56	61
1.0	51
1.8	46
9.5	44
10.2	50

butyllithium, and the apparent λ_{max} is shifted toward longer wavelengths. However, the ir spectrum of reacting solutions could not be distinguished from the spectrum of ketone 2 in the carbonyl stretching region. Only the band at 1690 cm⁻¹ was observed. The use of the more hindered ketone, 2,4-dimethyl-4'-methylmercaptobenzophenone (1), makes it possible to record several spectra during the course of the reaction. This is illustrated in Figure 1 for the reaction of 8 × 10⁻³ M n-butyllithium with 6.1 × 10⁻⁵ M ketone 1 in benzene at 25 °C. The rapid scan uv spectrum of this reaction, recorded 18.2 times per second (1), indicated that the absorbance remained broad as it disappeared.

The presence of enhanced absorbance at longer wavelengths in the uv spectrum noted here is similar to the development of a resolved new absorbance in both the uv and ir in the reaction of ketones with methylmagnesium bromide.[29] In the case of the Grignard reagent, the long-wavelength uv absorbance was attributed to a complex between the organomagnesium reagent and the carbonyl oxygen which was subsequently converted to product.[29]

The kinetics of the reaction of 4-methylmercaptoacetophenone with n-butyllithium in benzene were studied by stopped-flow spectroscopy. A typical run, recorded at 330 nm, is illustrated in Figure 2. The integrated first-order rate constant calculated from Figure 2 is summarized in Table I. The reaction is first order in ketone under these concentration conditions, as shown in Figure 2 and Table I. The observed first-order rate constant for the reaction 0.125 M n-butyllithium with 5.6 × 10⁻⁴ to 1.8 × 10⁻² M 4-methylmercaptoacetophenone in benzene at 25.0° was appropriately independent of the ketone concentration provided ketone was at least 10⁻³ M. A competing reaction, probably caused by alkoxides in the n-butyllithium reagent, caused k_{obsd} to be dependent on ketone concentration when ketone was less than 10⁻³ M (Table II).
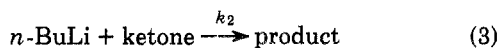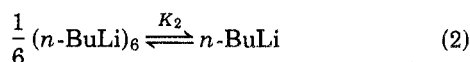
Figure 3 is a plot of the observed first-order rate constant, k_{obsd} (Table III), vs. n-butyllithium concentration, measured under the conditions of excess lithium reagent. This plot shows that the reaction is not first order in alkyllithium because the rate of the reaction increases rapidly as the concentration of n-butyllithium is increased from 0.014

Table III.   Summary of Observed Pseudo-First-Order Rate
Constants for the Reaction of *n*-Butyllithium with
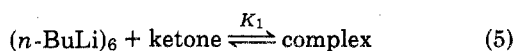4-Methylmercaptoacetophenone in Benzene at 25.0°C

10 *n*-butyllithium, M	10^3 ketone, M	k_{obsd}, s^{-1}
0.14	1.50	30
0.19	1.60	33
0.21	1.45	34
0.26	1.45	34
0.27	1.45	33
0.29	2.26	37
0.32	1.60	31
0.37	1.50	32
0.41	2.26	39
0.47	1.60	34
0.50	1.50	34
0.64	1.60	37
0.65	2.28	36
0.67	1.60	34
0.85	2.28	40
0.92	1.6	40
1.5	2.28	46
2.6	1.32	41
3.8	1.32	44
4.0	1.32	44
6.3	1.32	48
7.0	1.32	50
7.7	1.22	50
8.8	1.22	49

to ca. 0.1 M, but the rate is not greatly enhanced by further increases in lithium reagent concentration.

These data are consistent with either of the idealized cases of reaction predominantly through a less associated species than the hexamer, eq 2–4, as we found earlier for methyllithium in diethyl ether[2a] or by a mechanism involving a ketone lithium reagent complex as was found in the analogous reactions of Grignard reagents, eq 5–7[29] The

$$\frac{1}{6} (n\text{-BuLi})_6 \overset{K_2}{\rightleftharpoons} n\text{-BuLi} \tag{2}$$

$$n\text{-BuLi} + \text{ketone} \overset{k_2}{\longrightarrow} \text{product} \tag{3}$$

$$k_{obsd} = k_2 K_2 (n\text{-BuLi})_6^{1/6} \tag{4}$$

$$(n\text{-BuLi})_6 + \text{ketone} \overset{K_1}{\rightleftharpoons} \text{complex} \tag{5}$$

$$\text{complex} \overset{k_1}{\longrightarrow} \text{product} \tag{6}$$

$$k_{obsd} = \frac{k_1 K_1 (n\text{-BuLi})_6}{1 + k_1 (n\text{-BuLi})_6} \tag{7}$$

present data do not, of course, unambiguously distinguish between other fractional orders in butyllithium. However, the hexameric character of the butyllithium and the known one-fourth in the reaction of tetrameric methyllithium makes the one-sixth order a reasonable choice. The perturbation of the uv spectrum in the presence of *n*-butyllithium is consistent with the presence of complex; however, a quantitative assessment of its importance has not yet been possible because of considerable uncertainty in initial absorbance data which is attributed to variable amounts of alkoxide in different preparations of *n*-butyllithium. Other roles for a complex between *n*-butyllithium and the ketone in benzene suggested by the uv spectrum than the simple case outlined in eq 5–7 can be proposed. Furthermore, it should be noted that these equations suggest just one of many possible types of complex and pathway to product.

Trace amounts of lithium alkoxides were found to increase the rate of reaction of 4-methylmercaptoacetophenone with *n*-butyllithium (Table IV). For example, the addition of 0.001 M of the product alcohol to 0.1 M butyllithi-
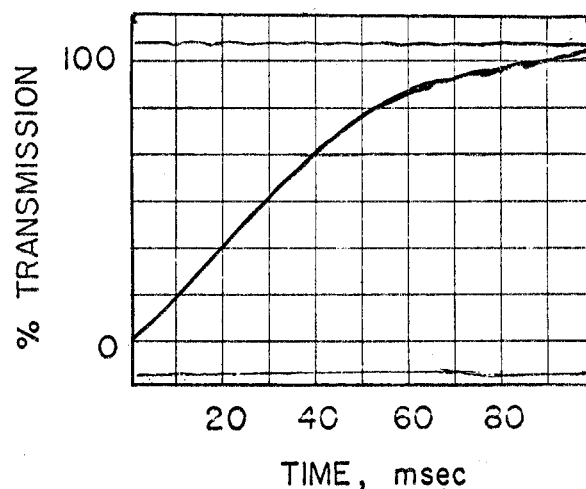

Figure 2. Plot of percent transmission vs. time for the reaction of 0.13 M *n*-butyllithium with 1.3 × 10^{-3} M 4-methylmercaptoacetophenone in benzene at 25.0 °C, recorded at 330 nm.
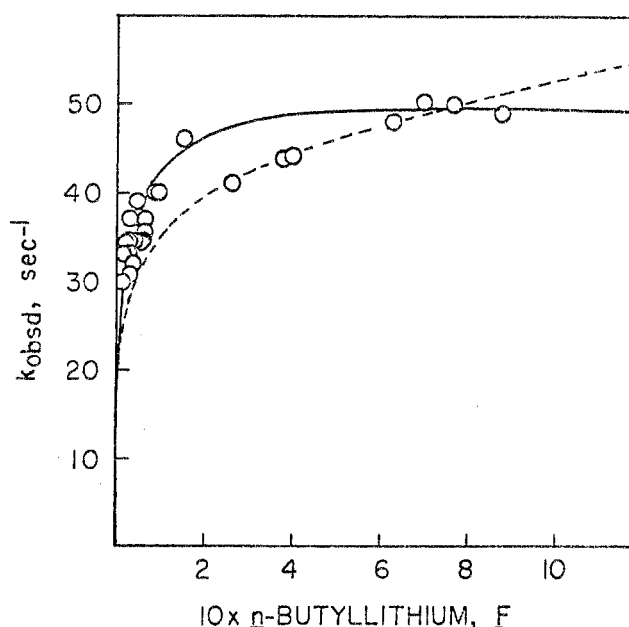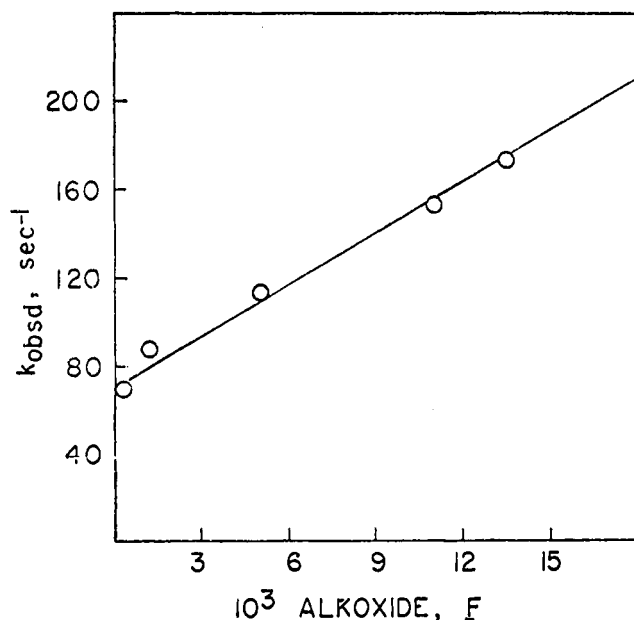

Figure 3. Plot of observed pseudo-first-order rate constant vs. *n*-butyllithium for the reaction of *n*-butyllithium with 1.22 to 2.28 × 10^{-3} M 4-methylmercaptoacetophenone in benzene at 25.0 °C, Table II. The solid line is calculated from eq 7 with $K_1 = 600$ and $k_1 = 50$. The dotted line is calculated from eq 4 with $k_2 K_2 = 70$.

um increases the measured first-order rate constant by a factor of about 2. However, if the alkoxide is generated by addition of alcohol to the ketone so that alkoxide is formed upon rapid mixing with the lithium reagent in the stopped flow apparatus, the reaction is found to be independent of alkoxide concentration (Table V). Alkoxide is, of course, also generated during the course of the reaction by the addition of the lithium reagent to the carbonyl group. However, even with 0.01 M ketone, the reaction was not autocatalytic within the accuracy of the measurements.

The failure of alkoxide generated during the reaction to have the same accelerating effect as that of alkoxide added to the lithium reagent prior to the addition of the ketone suggests that the rate of addition to the carbonyl group of ketone is fast relative to the equilibration of the lithium alkoxide with *n*-butyllithium which produces the species responsible for the enhanced reactivity. This is consistent with available data on intermolecular exchange of ethyllithium in toluene,[30-32] which shows an exchange time of ca.

Figure 4. Plot of observed rate constant vs. the concentration of lithium 2-(4-methylmercaptophenyl)-2-hexoxide for the reaction of 0.15 M n-butyllithium with 5.75 × 10^{-4} M 4-methylmercaptoacetophenone, in the presence of lithium 2-(4-methylmercaptophenyl)-2-hexoxide, in benzene at 25.0 °C.

0.1 s at room temperature, which is slow compared to the rate of addition of n-butyllithium to ketone 2. However, it is clear that more information on the composition and rates of equilibration of n-butyllithium solution containing alkoxides is needed to further clarify the course of the reaction.

The products of the reaction of 4-methylmercaptoacetophenone with n-butyllithium were analyzed under conditions employed in the kinetic study. A sample of ketone 2, containing biphenyl as an internal standard, was mixed with n-butyllithium in benzene in a stopped-flow apparatus. The stopped-flow effluent was quenched with ice, acidified to pH 7, then analyzed by GLC. The GLC chromatogram consisted of three peaks with retention times identical with those of the addition alcohol, 2-(4-methylmercaptophenyl)-2-hexanol, and small amounts of the alcohol dehydration products, 2-(4-methylmercaptophenyl)-2-hexene and 2-(4-methylmercaptophenyl)-1-hexene. The pinacol of ketone 2, which was not eluted from the GLC column, was not detected by thin layer chromatography, indicating that less than 1.5% of the pinacol was present since 1.5% of the pinacol in a control sample was detected.

Product studies of the reaction of n-butyllithium–alkoxide mixtures with 4-methylmercaptoacetophenone and of the reaction of n-butyllithium with 4-methylmercaptoacetophenone containing product alcohol were performed under the reaction conditions employed in the kinetic studies. In all cases, only the addition product alcohol, 2-(4-methylmercaptophenyl)-2-hexanol, was found by GLC analysis, using biphenyl as the internal standard.

Experimental Section

n-Butyllithium. n-Butyllithium was prepared from Foote Mineral Co. Reactor Grade lithium (99.99% Li) and degassed freshly distilled n-butyl chloride on a vacuum line that was under a positive pressure of argon. Lithium chips were cut in an argon atmosphere, under mineral oil, and then the oily pieces were transferred to the vacuum line. After evacuating and flushing the vacuum line with argon, the lithium chips were washed three times with benzene solution, and the washings were expelled from the vacuum line. Fresh benzene was admitted to the reaction vessel and the halide was slowly added over ca. 1 h, while the reaction was main-

Table IV. Summary of Observed Pseudo-First-Order Rate Constants for the Reaction of 0.15M n-Butyllithium with 5.8 × 10^{-4} M 4-Methylmercaptoacetophenone in the Presence of Lithium 2-(4-Methylmercaptophenyl)-2-hexoxide, in Benzene at 25.0° C

10^3 alkoxide, M	k_{obsd}, s^{-1}
0.35	70
1.2	88
5.0	113
11.0	153
13.5	174

Table V. Effect of Product Alkoxide on the Reaction of 0.151 M n-Butyllithium with 10^{-3} M 4-Methylmercaptoacetophenone in Benzene at 25.0°C

10^3 alkoxide[a]	k_{obsd}, s^{-1}
1.27	50
2.23	56
5.97	53
9.68	54

[a] Alkoxide formed by reaction of 2-(4-methylmercaptophenyl)-2-hexanol, contained in the ketone solution, with n-butyllithium in the stopped-flow apparatus.

tained at room temperature. The reaction mixture was allowed to stir for ca. 12 h after the halide addition was complete. The reagent was filtered twice through glass fritted filters and transferred via argon pressure into silicon rubber septum topped vials. The samples were used within 2 h after they were removed from the vacuum line, and titrated within 8 h after use.

n-Butyllithium reagents were analyzed by total base titration with standard standardized hydrochloric acid solutions. The lithium reagent content, analyzed with standard solutions of sec-butyl alcohol in xylene containing 1,10-phenanthroline as an indicator, agreed with the total base titer. Tared vials used in kinetic experiments were weighed to determine the amount of n-butyllithium–benzene solution they contained. Then the titration mixture, which was stored under argon, was admitted to vials via a syringe needle on a microburet. A red-orange alkyllithium indicator complex forms and when all lithium reagent has been converted to lithium sec-butoxide, the solution becomes lime green.[33]

Alkoxide concentrations were calculated from the weight of alcohol added to the reagent vials. The alcohols were vacuum dried for at least 1 day before n-butyllithium solutions were added.

4-Methylmercaptoacetophenone. The preparation of 4-methylmercaptoacetophenone has been described elsewhere.[29] Alternatively,[34] the ketone was prepared by placing 0.26 mol (31 ml) of thioanisole and 0.48 mol (100 g) of trifluoroacetic anhydride in a 1-l. flask equipped with magnetic stirrer, condenser, addition funnel, and nitrogen inlet. The flask was cooled in an ice bath and 0.38 mol (23 ml) of acetic acid was added. The mixture was extracted with ether, and the ether was subsequently washed with bicarbonate and water. The ether was dried over sodium sulfate and removed from the product on a rotary evaporator. The resulting orange crystals were purified by distillation at 125 °C and 0.05 mm pressure. The white, crystalline distillate was recrystallized once from hexane, giving 22.1 g of crystals (51%), mp 80.5–81.5 °C.

The concentrations of ketone samples used in kinetic studies were calculated from the weight of ketone and the weight of added solvent. The ketone dried on a vacuum line (0.05 mm) for at least 1 day before freshly distilled solvent was added to the vials.

2,3-Dimethyl-4'-methylmercaptobenzophenone. The preparation of 2,4-dimethyl-4'-methylmercaptobenzophenone has been described elsewhere.[29c]

2-(4-Methylmercaptophenyl)-2-hexanol. A 2-l. flask was equipped with a magnetic stirrer, syringe port, dropping funnel, condenser, and argon inlet. Benzene (350 ml) dried over 4-A molecular sieves, was added to the flask; then 150 ml of 1.3 N n-butyllithium in hexane (Foote Mineral Co.) was added through the syringe port. Ten grams of 4-methylmercaptoacetophenone in 200 ml of benzene was added to the flask over a 45-min period. After standing overnight the reaction mixture was quenched with water and neutralized with dilute sulfuric acid. The layers were separated, and the hydrocarbon layer was washed with 2 × 50 ml of

aqueous potassium carbonate solution and 3 × 150 ml of water and dried over sodium sulfate. The solvent was removed on a rotary evaporator, yielding a viscous brown oil. Distillation at 0.75 mm through a short-path micro distillation head yielded 7 ml of a pale yellow oil containing some starting ketone, and 3 ml of oil free of ketone: ir (CCl$_4$) 3430 cm^{-1} (–OH); NMR (CCl$_4$) δ 7.15 (m, 4, Ar), 2.6 (s, 1, –OH), 2.32 (s, 3, CH$_3$S–), 0.6–1.9 (m, 12, alkyl). Anal. Calcd for C$_{13}$H$_{20}$OS: C, 69.50; H, 8.99; S, 14.29. Found: C, 68.94; H, 8.95; S, 13.87.

2,3-Di(4-methylmercaptophenyl)-2,3-butanediol. 4-Methylmercaptoacetophenone (10 g) was dissolved in 75 ml of absolute ethanol and 50 ml of benzene. Aluminum foil (3 g), cut in 0.5-in. squares, was added to the solution. Mercuric chloride (0.15 g) was added to the mixture, and then the reaction mixture was stirred and cooled to ice-bath temperature as described by Sisido and Nozaki.[35]

The flask was allowed to warm, and an exothermic reaction began, causing the reaction to reflux for approximately 1 h. The mixture was heated to reflux for an additional 1 h. The resulting gray viscous mixture was poured onto ice and neutralized with dilute hydrochloric acid. The benzene layer was separated from the aqueous phase, combined with benzene extracts of the aqueous phase, and dried over sodium sulfate. The solvent was removed on a rotary evaporator. The resulting solid was recrystallized twice from benzene (69% yield): mp 127–129; ir (CCl$_4$) 3600 cm^{-1} (–OH); NMR (CCl$_4$) δ 7.08. Anal. Calcd for C$_{18}$H$_{22}$O$_2$S$_2$: C, 64.63; H, 6.63; S, 19.17; O, 9.57. Found: C, 64.36; H, 6.45; S, 19.24; O, 9.95 by difference.

Product Studies. A 1.8 × 10^{-2} M solution of 4-methylmercaptoacetophenone in benzene, containing biphenyl in the molar ratio ketone/biphenyl 1.23, was mixed with a 0.27 M solution of n-butyllithium in a stopped-flow apparatus. The effluent of the stopped-flow instrument was quenched with ice so that the time of reaction was less than 1 min. The ice–benzene mixture was warmed to room temperature and titrated to pH 6 with dilute sulfuric acid. The benzene layer was then separated, combined with an ether extract of the aqueous phase, and dried over sodium sulfate. Solvent was removed by gently boiling off ether on a steam bath, then by bubbling dry nitrogen through the solution overnight. Quantitative GLC analysis, with biphenyl as the standard, on a 2-m 20% Carbowax 20M on Chromosorb W column indicated that the addition product was formed in 99% yield. Less than 1% of the addition product had dehydrated. No evidence for ketone reduction or enolization was found by this procedure, placing the limits of these products at 2%. No evidence for ketone dimerization product was found when the reaction product was analyzed on a 2-m, 1.5% SE-30 on Fluorapak 80 column or by thin layer chromatography. The limit of detection by the TLC method was ca. 1.5%. A 10^{-2} M ketone solution, containing triphenylmethanol in the ratio ketone/Ph$_3$COH 2.595, was treated with 0 18 M n-butyllithium solution. GLC analysis indicated that only addition product was formed. Similarly, a 10^{-2} M ketone solution containing the ketone dimerization product in the ratio ketone/pinacol 71.24 was found to yield only addition product. A 10^{-2} M ketone solution was allowed to react with a 0.18 M n-butyllithium solution that was saturated

with the lithium salt of triphenylmethanol and found to yield only addition product.

Kinetics and Spectroscopy. The two uv stopped-flow spectrophotometers with dead times of 0.03 and 0.001 s as well as the rapid-scan spectrometer have been described elsewhere.[2,29b] The stopped-flow ir spectrophotometric experiments were performed with the apparatus previously described;[29a] however, the ir chopping frequency has been increased to ca. 10 000 Hz.

References and Notes

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