Mechanism of Reaction of Carbon Monoxide with Phenyllithium

Larry S. Trzupek, Terry L. Newirth, Edward G. Kelly, Norma Ethyl Sharbati, and George M. Whitesides*

Contribution from the Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139. Received July 14, 1973

Abstract: The product mixtures obtained by reaction between phenyllithium and carbon monoxide in diethyl ether, followed by hydrolysis, include benzophenone (1), \(\alpha,\alpha\)-diphenylacetonaphone (2), benzil (3), \(\alpha,\alpha\)-diphenyl-\(\alpha\)-hydroxycetophenone (4), benzpinacol (5), \(\alpha\)-hydroxycetophenone (6), 1,3,3-triphenylpropane-1,2-dione (7), 1,3,3-triphenylpropan-1-one-2,3-diol (8), and benzhydryl (9). Compounds 1, 2, 6, 7, and 8 are produced in significant yields; 3, 4, 5, and 9 are produced in trace quantities. Spectroscopic studies establish dilithium benzophenone dianion (18) as the first long-lived intermediate formed in this reaction; qualitative correlations between the basicity of a number of organolithium reagents and their reactivity toward carbon monoxide suggests, but does not prove, that benzylithium is a precursor of 18. Labeling experiments indicate that the products ultimately isolated following hydrolysis of the reaction mixture are derived from at least two pathways which compete for the initially formed 18. One involves combination of 18 with 1 equiv of phenyllithium and 1 equiv of carbon monoxide, followed by elimination of 1 equiv of lithium oxide, yielding 17, the lithium enolate of 2; a second involves combination of 18 with 1 equiv of phenyllithium and 2 equiv of carbon monoxide, yielding 22, the trilithium trianion of 8. Hydrolysis of 17 yields 2 directly. Hydrolysis of 22 yields 8; reverse aldol reactions involving 8 or its precursors generate 1 and 6. The mechanism proposed to account for the major products of the reaction of phenyllithium and carbon monoxide is outlined in Scheme III. On the basis of this scheme, plausible paths to the minor products of the reaction are proposed.

The addition of nucleophiles to carbon monoxide, activated by coordination to metal ions, forms the basis for a thoroughly explored and useful class of reactions. Transformations related to the hydroformylation process, additions of organolithium reagents to metal carbonyls, carboxylation of mercury(II) salts, organoboranes, and organocopper reagents, metal-catalyzed oxidative coupling of amines with carbon monoxide, and metal-catalyzed oxidation of carbon monoxide in aqueous solution, each involve the attack of formally anionic groups on metal-coordinated carbon monoxide. Acylmetallic compounds have either been inferred or identified as intermediates in many of these reactions, and this class of substance provides the foundation for discussions of their mechanisms.

The reactions of nucleophiles with free or weakly coordinated carbon monoxide are less well understood. Base-catalyzed carbonylation of alcohols and amines, and the reactions of organolithium, catalyzed oxidative coupling of amines with carbon monoxide, and metal-catalyzed oxidation of carbon monoxide in aqueous solution, each involve the attack of formally anionic groups on metal-coordinated carbon monoxide. Acylmetallic compounds have either been inferred or identified as intermediates in many of these reactions, and this class of substance provides the foundation for discussions of their mechanisms.

(1) Supported by the National Institutes of Health, Grants GM 16020 and HL-15029, and by the U. S. Army Research Office (Durham), Grant ARO-D-31-124-G69.
(2) National Science Foundation Trainee, 1968-1969.

magnesium,14-17 sodium,18,19 and zinc20 reagents with carbon monoxide require nucleophilic attack on carbon monoxide in the absence of the obvious activation provided by coordinating transition metal ions. Stable acyl derivatives of group Ia and Ila metal ions are not well-characterized entities, although they have been implicated in reactions between carbon monoxide and tert-butylithium,21 trimethylsilylithium,22 and various lithium amides.23,24

The work reported in this paper was initiated in the hope that a study of the reaction of carbon monoxide with phenyllithium would provide evidence bearing both on the stability of acylithium compounds and on the mechanisms of the reactions between organometallic nucleophilic acyl groups.25 In fact, no evidence for long-lived acylithium compounds as intermediates in the mechanisms of the reactions between organometallic hope that a study of the reaction of carbon monoxide with benzophenone ketyl, benzophenone dianion, and related materials, and suggest new ways in which carbon monoxide might be used in synthesis.

Results

Products. At −78°C, phenyllithium in diethyl ether solution reacts over ca. 6 hr with carbon monoxide at 1 atm pressure; reaction at 0°C is complete in 3–4 hr. The phenyllithium solutions used in most of the reactions in this study were obtained by reaction of bromobenzene with lithium metal and contained lithium bromide;26 the reactions of these solutions with carbon monoxide were homogeneous throughout. Carboxylation of analogous lithium halide free solutions of phenyllithium, prepared by transmetallation of dibenzylmagnesium,27 gave similar product distributions but were heterogeneous in the latter stages of reaction. The quantity of carbon monoxide absorbed when the reactions were allowed to proceed to completion varied with reaction conditions, but typically 0.8–1.0 equiv of carbon monoxide was consumed per equivalent of phenyllithium. Hydrolysis and glpc analysis of the reaction mixtures led to identification of a number of products: benzophenone (1), α,α-diphenylacetophenone (2), benzil (3), α,α-diphenyl-α-hydroxyacetophenone (4), and traces of benzoin (5) and benzhydrol (9). Careful thin-layer chromatography of the nonvolatile products of the hydrolysis permitted isolation of α-hydroxyacetophenone (6) and two compounds assigned the structures 1,2,3-triphenyl-1,2-propanediol (7) and 1,3,3-triphenyl-2,3-dihydroxy-1-propanone (8) on the basis of evidence outlined below. Certain of these products, or benzene in pentane solution,28 gave similar product distributions but were heterogeneous in the latter stages of reaction. The quantity of carbon monoxide absorbed when the reactions were allowed to proceed to completion varied with reaction conditions, but typically 0.8–1.0 equiv of carbon monoxide was consumed per equivalent of phenyllithium.

\[
\begin{align*}
\text{PhLi} & \quad \text{CO (1 atm), Et}_2\text{O} \quad \text{PhC} - \text{Ph} + \text{PhCClPh}_2 + \\
\text{PhC} - \text{Ph} + \text{PhCClPh}_2 & \quad \text{PhCClOH} + \text{PhCCHPh}_2 + \\
\text{PhCClPh}_2 & \quad \text{PhCClPh}_2 + \text{PhC} - \text{Ph}
\end{align*}
\]

1. CO (1 atm), Et₂O
2. H₂O
3. O
4. OH OH
5. O
6. O
7. OOH OH OH
8. PhCClPh₂ PhCClPh₂ PhCClPh₂ PhCClPh₂

PhCClPh₂ PhCClPh₂ PhCClPh₂

1. CO (1 atm), Et₂O
2. Ac₂O
3. Ph
4. Ph
5. Ph
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7. Ph
8. Ph

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24) The structurally related lithium aldimes are stable at low temperature, L1 at low temperature.
in the reaction of phenyllithium with carbon monoxide in ether. Yields of 1-5 in the first four entries in the table were obtained using unexceptional glpc techniques. The yields of 1 and 6 in the last entry were obtained by isotopic dilution, using a combination of tlc and mass spectroscopic techniques. Compounds 6, 7, and 8 could not be assayed directly by any glpc technique we were able to devise. Instead, phenyl-d5-lithium was allowed to react to completion with carbon monoxide, and the reaction mixture was hydrolyzed. Known quantities of deuterated 1, 6, 7, and 8 were added to the reaction mixture, and the resulting mixture of deuterated and nondeuterated materials was separated by preparative tlc. The yields of products in the reaction of the phenyl-d5-lithium with carbon monoxide were estimated on the basis of the results of mass spectral analysis of the isotopic composition of these mixtures. The difference in the yields of 1 observed at -70°C using glpc and isotopic dilution analyses is easily rationalized on the assumption that 8 decomposes in part to 1 in the glpc injection port (vide infra).

The necessity for using isotopic dilution techniques to determine yields of 6, 7, and 8 rendered product distribution studies too laborious to be a practical method of approaching a study of the mechanism of this reaction. Further, product distributions were difficult to reproduce in detail, and product balances greater than 80% were achieved only under special circumstances. Nonetheless, two qualitative features of the observed product distributions are experimentally significant and pertinent to the mechanistic discussions that follow. First, the yields of 1 and 2 vary in a reproducible way with temperature: 2 dominates at room temperature; 1 dominates at low temperature. Second, the yields of 1-5 (and presumably 6-8) are relatively insensitive to changes in reaction conditions other than temperature: addition of dimethoxyethane (DME) or N,N,N',N'-tetramethylethylenediamine (TMEDA) to these ethereal reaction solutions results in an increase in the yield of benzil (3) to ca. 10% with decreases of the same magnitude in the yields of 1 and 2; substituting solutions of lithium halide-free phenyllithium for the lithium halide-containing solutions usually used or changing the concentration of phenyl-

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Scheme I. Synthesis of Authentic Samples of Products

Table I. Product Yields (%) from the Reaction of Phenyllithium with Carbon Monoxide in Diethyl Ether

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In the reaction of phenyllithium with carbon monoxide in ether. Yields of 1-5 in the first four entries in the table were obtained using unexceptional glpc techniques. The yields of 1 and 6 in the last entry were obtained by isotopic dilution, using a combination of tlc and mass spectroscopic techniques. Compounds 6, 7, and 8 could not be assayed directly by any glpc technique we were able to devise. Instead, phenyl-d5-lithium was allowed to react to completion with carbon monoxide, and the reaction mixture was hydrolyzed. Known quantities of deuterated 1, 6, 7, and 8 were added to the reaction mixture, and the resulting mixture of deuterated and nondeuterated materials was separated by preparative tlc. The yields of products in the reaction of the phenyl-d5-lithium with carbon monoxide were estimated on the basis of the results of mass spectral analysis of the isotopic composition of these mixtures. The difference in the yields of 1 observed at -70°C using glpc and isotopic dilution analyses is easily rationalized on the assumption that 8 decomposes in part to 1 in the glpc injection port (vide infra).

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lithium by a factor of 5, resulted only in small changes in yields. In no cases were new products detected.

In an effort to establish the fate of the phenyl groups that do not appear among the characterized products of the reaction, several reaction mixtures were explicitly examined for the presence of a number of compounds which might plausibly have been produced. Careful analyses of representative reaction mixtures demonstrated that benzene, benzoic acid, benzaldehyde, benzyl alcohol, biphenyl, triphenylmethane, triphenylcarbinol, and 1,1,2-triphenylethane-1,2-diol were not produced in detectable quantity. The observation that triphenylcarbinol is not a reaction product is of particular mechanistic significance. Since phenyllithium reacts readily with benzophenone, yielding triphenylcarbinol, under the conditions of these reactions, the absence of triphenylcarbinol as a product indicates that benzophenone does not appear in the reaction mixture until phenyllithium has been completely consumed. This conclusion was strengthened and extended by determining indirectly the quantity of benzophenone present in solution on completion of the reaction between phenyllithium and carbon monoxide before hydrolysis. An aliquot of a reaction solution that had been allowed to react to completion with carbon monoxide at room temperature was treated with lithium aluminum hydride. Since the benzophenone present before hydrolysis would have been reduced to benzhydrol by LiAlH4, this experiment establishes that the benzophenone observed as a product in these reactions is not present in the reaction mixture before hydrolysis.

One additional useful datum can be derived from studies of the products of the reaction; viz, since 1,2,2-triphenyl-1-acetoxyethylene (10) replaces 2 in room temperature reaction mixtures quenched with acetic anhydride, the immediate precursor of 2 before hydrolysis is probably the corresponding lithium enolate 11.

Similarly, the observation that 1, 6, and 7 are replaced by 11 on treatment of product mixtures obtained at low temperature suggests that these materials share a common precursor. Confirming this suggestion and identifying the structure of the precursor is one focus of the work that follows.

**Dilithium Benzophenone Dianion (18)** and **Lithium Benzophenone Ketyl (19).** The first substantial evidence concerning the nature of the intermediates in the reaction of phenyllithium and carbon monoxide emerged from spectroscopic studies of the striking color changes that characterize the reaction. Contact of carbon monoxide with phenyllithium in diethyl ether or ether-DME solutions produces an immediate intense red coloration in the solution, which persists throughout the greater part of the reaction. The final stages of reaction are characterized by a transition of the solution color from red to greenish brown.

Our initial attempts to identify the substance(s) responsible for the red color were guided by the hypothesis that benzophenone and other products containing diphenylmethyl moieties might be derived in some fashion from dilithium benzophenone dianion (18),

\[
\text{(PhLi)}_2 + \text{CO} \rightarrow \text{PhCPH}^\text{+} \rightarrow \text{PhCPH}^\text{2+}
\]

which forms deep red-purple solutions in ether solution, or from lithium benzophenone ketyl (19). In principle, carbon monoxide insertion into a phenyllithium dimer would yield 18; alternatively, carbon monoxide insertion into phenyllithium monomer could yield a transitory benzophenone species which could be converted into 18 by reaction with a second molecule of phenyllithium. One-electron oxidation could convert 18 to 19 and ultimately to benzophenone. In order to test this hypothesis, it was clearly necessary to have available authentic samples of 18 and 19. Although both 18 and 19 have been thoroughly studied in other circumstances, the techniques used for preparation of these species, and for their characterization and identification under the reaction conditions encountered in these studies, were not entirely straightforward and are outlined here.

Solutions of dilithium benzophenone dianion in DME were prepared by reduction of benzophenone with an excess of lithium dispersion. Solutions of 19 in DME were obtained by reduction of 1 equiv of benzophenone with 1 equiv of lithium dispersion, or by reaction of benzpinacol with excess methyl- or phenyllithium. Preparation of these materials in diethyl ether solution were carried out using similar
techniques, although the low solubilities of 18 and 19 in this solvent make their solutions particularly susceptible to accidental hydrolysis or oxidation.\textsuperscript{39}

Solutions were analyzed for 18 and 19 by taking advantage of the characteristic behavior of these materials on oxidation and hydrolysis. Both dilithium benzophenone dianion and lithium benzophenone ketyl are oxidized to benzophenone by molecular oxygen.\textsuperscript{33,34} Hydrolysis of dilithium benzophenone dianion yields benzhydrol: hydrolysis of benzophenone ketyl with aqueous base (pH >13) yields a 1:1 mixture of benzophenone and benzhydrol. Thus, in principle, comparison of the yields of benzophenone and benzhydrol obtained on oxidation and hydrolysis of aliquots of a solution containing 18 and 19 should provide a straightforward method of determining the concentrations of these species: the yield of benzophenone obtained on oxidation of the solution would reflect the combined quantities of 18 and 19 present; the yield of benzhydrol obtained on alkaline hydrolysis would correspond to one-half the quantity of 19 present. This analytical technique suffers, however, from two ambiguities. First, the extent to which the ketyl 19 is dimerized in solution, particularly at the relatively high concentrations used in this work, is unclear;\textsuperscript{40} thus, the yield of benzhydrol obtained on basic hydrolysis is probably best considered a measure of the total quantity of monomeric and dimeric 19 rather than a direct measure of monomeric 19 alone. Second, since it has not been possible to prepare samples of either 18 or 19 unambiguously, it has not been possible to prove that either hydrolysis or oxidation lead quantitatively to the indicated products. Thus the concentrations for 18 and 19 inferred from these analyses should be taken as minimum values. Nonetheless, several experimental observations suggest that determination of the relative yields of benzophenone and benzhydrol obtained following hydrolysis and oxidation of a solution containing 18 and 19 does in fact provide a reasonably accurate method for determining the concentrations of these compounds. First, the yields of benzophenone and benzhydrol observed on oxidation or hydrolysis of solutions of 18 and 19 prepared by reduction of benzophenone with appropriate quantities of lithium metal account for 85–100\% of the starting material (Table II). Further, the product balances obtained on hydrolysis and oxidation of aliquots of a common solution agree well. Thus, it appears that both reactions take place in high yield. Second, the ratio of benzhydrol to benzophenone obtained on hydrolysis of solutions ostensibly containing benzophenone dianion is <0.01, while this ratio for solutions ostensibly containing benzophenone ketyl ranges from 0.87–0.95, in reasonable agreement with the expected value of 1.00. Third, the spectroscopic examinations described below establish that reduction of benzophenone with 1 equiv of lithium yields a solution which contains benzophenone ketyl but little if any benzophenone dianion and that continued reduction using an excess of lithium yields solutions containing benzophenone dianion but little benzophenone ketyl. Taken together, these results indicate that reduction of even high concentrations of benzophenone with appropriate quantities of lithium metal in ethereal solvents yields solutions containing 18 and 19 in good yield, uncontaminated by important quantities of other materials, and that comparison of the yields obtained in the latter solution is ~10\% vol.\textsuperscript{1} J. Garst, D. Walmsey, C. Hewitt, W. Richards, and E. Zabolotny, ibid., 86, 412 (1964). Magnetic susceptibility measurements indicate that sodium benzophenone ketyl is >99\% associated to a diamagnetic form in benzene: R. N. Doescher and G. W. Wheland, ibid., 56, 2011 (1934).

\textsuperscript{39} Solubility of both 18 and 19 in ethereal solvents is limited: 18 appears to precipitate from solutions of DME at ambient temperatures at concentrations \(>0.0065\) M; the limiting solubility of 19 in DME is \(<0.006\) M in EtO it is \(<0.003\) M.

\textsuperscript{40} Although 19 is apparently monomeric in dioxane solution at \(10^{-4}-10^{-5}\) M concentrations,\textsuperscript{11} its visible absorption in diethyl ether shows significant deviations from Beer's law.\textsuperscript{14} No benzpinacol is observed on hydrolysis of 19 under basic conditions, in agreement with earlier work;\textsuperscript{11,30} nonetheless, because benzpinacol is rapidly cleaved and S. I. Weissman, J. Amer. Chem. Soc., 86, 2538 (1964), See also D. J. Morantz and E. Warhurst, ibid., 51 ,1375 (1955); N. Hirota and S. I. Weissman, J. Amer. Chem. Soc., 86, 2538 (1964). See also D. J. Morantz and E. Warhurst, ibid., 51, 1375 (1955); N. Hirota and S. I. Weissman, J. Amer. Chem. Soc., 86, 2538 (1964).


of benzophenone and benzhydrol obtained on oxidation and hydrolysis of these solutions provides a practical method of analyzing for these substances.

Spectroscopic Studies. The procedures described were used to prepare samples of 18 and 19 whose uv and visible spectra could be compared with those from solutions obtained on reaction of phenyllithium with carbon monoxide. The spectra of 18 and 19 are strongly dependent on concentration, on the nature and concentration of associated metal ions, and on the polarity of the solvent. In order to obtain spectra of 18 and 19 that could be compared directly with spectra taken in the initial stages of reactions between phenyllithium and carbon monoxide, we carried out spectroscopic studies of authentic solutions of 18 and 19 in ethereal solutions containing approximately 0.1 M phenyllithium. The use of phenyllithium solution as solvent has the additional practical advantage of minimizing the effects of adventitious traces of oxygen or water on the spectra of the benzophenone ketyls and di- and anions by acting as a scavenger for materials which would react with these organometallic reagents. The spectrum of phenyllithium itself does not interfere with those of the compounds of interest at wavelengths longer than approximately 300 nm. Visible spectra for dilithium benzophenone dianion and lithium benzophenone ketyl in 0.1 M solutions of phenyllithium in DME are given in Figure 1. The spectra of 18 were obtained with solutions prepared by dilution of concentrated stock solution to ~10⁻³ M: the spectra of 19 were obtained from solutions prepared by a similar dilution procedure or directly by reaction of benzpinacol with phenyllithium solution in the cuvette. For comparison, this figure also gives spectra of several compounds that either are themselves formed in significant concentration during the reaction (the lithium enolates of α,α-diphenylacetoephene (17) and 1,1,3-triphenylpropane-1,2-dione (15)) or that are spectroscopic models for compounds that are formed during the reaction (the dilithium dianion of 1-phenyl-3,3-dimethylbutane-1,2-dione (20) which is used as a model for the trilithium salt of 8). Absorption maxima and extinction coefficients (when estimated) obtained from these spectra are summarized in Table III. The phenyllithium used was that present in the solvent.

Table III. Absorption Maxima and Extinction Coefficients for Organometallic Species

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<th>Compound</th>
<th>Method of preparation</th>
<th>Solvent</th>
<th>λ max, nm</th>
<th>ε</th>
</tr>
</thead>
<tbody>
<tr>
<td>PhCOC(OLi)=CPh₃ (15)</td>
<td>PH₃C—CHCOPh + LiTMP</td>
<td>Et₂O</td>
<td>417</td>
<td>10⁰⁴</td>
</tr>
<tr>
<td>PhCOC(OLi)=CPh₃ (17)</td>
<td>PH₃C—C(OAc)Ph + PhLi⁺</td>
<td>DME</td>
<td>288</td>
<td>440,000</td>
</tr>
<tr>
<td>PhCOLi (18)</td>
<td>PH₃CO + Li</td>
<td>Et₂O</td>
<td>494</td>
<td>25,000</td>
</tr>
<tr>
<td>PhCOLi (19)</td>
<td>(Ph₂COH)₂ + PhLi⁺</td>
<td>DME</td>
<td>535</td>
<td></td>
</tr>
<tr>
<td>PhCOC(OLi)=C(OLi)(CCH₃) (20)</td>
<td>PhCOCOC(C(CH₃)₂ + excess lithium</td>
<td>DME</td>
<td>634</td>
<td></td>
</tr>
<tr>
<td>PhCOLi</td>
<td>PhCOCH + PhLi⁺</td>
<td>DME</td>
<td>300</td>
<td></td>
</tr>
</tbody>
</table>

Solutions were 0.1 N in phenyllithium. The literature values for the extinction coefficient of trityllithium in tetrahydrofuran is log ε 3.97 (425 nm). The phenyllithium used was that present in the solvent.

Figure 1. Ultraviolet-visible spectra of organometallic species in DME solution: (a) the reaction mixture obtained by adding phenyllithium to an excess of carbon monoxide dissolved in DME; (b) the reaction mixture obtained by adding carbon monoxide to a large excess of phenyllithium dissolved in DME; (c) Ph₃CLi; (15) PhCOC(OLi)=CPh₃; (17) PhCOC(OLi)Ph; (20) PhCOC(OLi)=ClOLi). The spectrum of phenyllithium itself does not interfere with those of the compounds of interest at wavelengths longer than approximately 300 nm. Visible spectra could be compared with those from solutions obtained on reaction of phenyllithium with carbon monoxide. The spectra of 18 and 19 are strongly dependent on concentration, on the nature and concentration of associated metal ions, and on the polarity of the solvent. In order to obtain spectra of 18 and 19 that could be compared directly with spectra taken in the initial stages of reactions between phenyllithium and carbon monoxide, we carried out spectroscopic studies of authentic solutions of 18 and 19 in ethereal solutions containing approximately 0.1 M phenyllithium. The use of phenyllithium solution as solvent has the additional practical advantage of minimizing the effects of adventitious traces of oxygen or water on the spectra of the benzophenone ketyls and di- and anions by acting as a scavenger for materials which would react with these organometallic reagents. The spectrum of phenyllithium itself does not interfere with those of the compounds of interest at wavelengths longer than approximately 300 nm. Visible spectra for dilithium benzophenone dianion and lithium benzophenone ketyl in 0.1 M solutions of phenyllithium in DME are given in Figure 1. The spectra of 18 were obtained with solutions prepared by dilution of concentrated stock solution to ~10⁻³ M: the spectra of 19 were obtained from solutions prepared by a similar dilution procedure or directly by reaction of benzpinacol with phenyllithium solution in the cuvette. For comparison, this figure also gives spectra of several compounds that either are themselves formed in significant concentration during the reaction (the lithium enolates of α,α-diphenylacetoephene (17) and 1,1,3-triphenylpropane-1,2-dione (15)) or that are spectroscopic models for compounds that are formed during the reaction (the dilithium dianion of 1-phenyl-3,3-dimethylbutane-1,2-dione (20) which is used as a model for the trilithium salt of 8). Absorption maxima and extinction coefficients (when estimated) obtained from these spectra are summarized in Table III. The phenyllithium used was that present in the solvent.

Table III. Absorption Maxima and Extinction Coefficients for Organometallic Species

<table>
<thead>
<tr>
<th>Compound</th>
<th>Method of preparation</th>
<th>Solvent</th>
<th>λ max, nm</th>
<th>ε</th>
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<td>300</td>
<td></td>
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Reactions of Dilithium Benzophenone Dianion with Carbon Monoxide in the Presence of Phenyllithium.

Although these spectroscopic studies implicate dilithium benzophenone dianion as the principal substance generated in the initial stage of these reactions, it remained to establish the role of this compound in the formation of the products actually isolated as their conclusion. In particular, it was important to know whether the lithium enolate of \( \alpha,\alpha\)-diphenylacetophenone (17) observed as the major reaction product at room temperature was derived from 18 or from phenyllithium by some reaction path not involving 18 and to determine whether 18 could plausibly give rise to benzophenone, the major low-temperature product, under the reaction conditions used in this work.

It was possible to establish by simple labeling experiments that the benzophenone moiety of benzophenone dianion was incorporated into both high- and low-temperature products on reaction with phenyllithium and carbon monoxide. For this purpose, we used 4,4'-di-tert-butylbenzophenone (23) as the labeled benzophenone rather than \(^{1}H\) or \(^{13}C\)-labeled material, because the dilithium dianion, 24, of this substituted benzophenone was much more soluble in ethereal solvents, and hence easier to prepare and manipulate, than was dilithium benzophenone dianion itself. Reaction of 24 with carbon monoxide in the presence of a tenfold excess of phenyllithium, followed by quenching of the reaction mixture with acetic anhydride, led to substantial incorporations (~60%) of the labeled benzophenone moiety into the products 25 and 26, the expected analogs of 10 and 11; yields of 10, 11, 25, and 26 obtained in several reactions are summarized in

(46) To establish that these results were independent of the method of labeling the reaction partners, similar although less accurate studies were carried out involving ethereal solutions containing 1 equiv of dilithium benzophenone dianion and 5 equiv of \( p \)-ethylphenyllithium. Exposure of these solutions to carbon monoxide, followed by hydrolysis, led to \( \alpha,\alpha\)-diphenyl-\( p \)-ethylacetophenone (iii) in 24% yield,

Table IV. An authentic sample of 26 was prepared by substitution of 4,4'-di-tert-butylbenzophenone for benzophenone in the procedures summarized in Scheme I: authentic 25 was synthesized by the procedure outlined in Scheme II.

The important conclusion from these spectroscopic experiments is that dilithium benzophenone dianion 18 is formed at the outset of the reaction of phenyllithium with carbon monoxide. Lithium benzophenone ketyl may be present in the reaction mixture late in the reaction.

To lend further support to the contention that 18 is present in reacting mixtures of phenyllithium and carbon monoxide, a 1 M solution of phenyllithium was stirred under 1 atm of carbon monoxide for 20 min and then quenched by addition of NaOD in D,O. Analysis by glpc and mass spectral analysis after the usual workup indicated the presence of 0.8% benzhydryl, containing >0.8 deuterium atoms per molecule.

The important conclusion from these spectroscopic
The mechanism for conversion of the diarylmethylene moiety of 24 to 26 is clearly more complex than that for the transformation of 24 to 25. Combination of 1 equiv of dianion 24, 2 equiv of carbon monoxide, and 1 equiv of phenyllithium in a process analogous to that required to form 27 would generate the trianion 28, the labeled analog of 22. Acylation of this substance with acetic anhydride, followed by loss of the oxygen originally present in 24, would in turn yield 26. Since the acetoxy group required to leave in this last step is activated toward heterolysis by two adjacent phenyl groups and one oxygen-substituted β-styryl moiety, sufficiently rapid conversion of 29 to 26 to preclude isolation of 29 would not be surprising; however, alternative schemes for conversion of 28 to 26 involving, e.g., monoaclylation of the oxygen derived from 27 followed by rapid loss of acetate ion, can of course also be written. We have no direct evidence for 29 or related species in these reactions, but the postulation of 28 as an intermediate is immediately compatible with the formation of compounds 1, 6, 7, and 8 as hydrolysis products from the reaction of phenyllithium and carbon monoxide by protonation, dehydration, and reverse aldol reactions, starting from the analogous trianion 22. The difference in the observed yields of 1 and 6 from

\[ \text{PhLi} + \text{CH}_2=\text{CHCl} \rightarrow \text{PhCHClCH}_2\text{Cl} \]

The mechanism for conversion of the diarylmethylene moiety of 24 to 26 is clearly more complex than that for the transformation of 24 to 25. Combination of 1 equiv of dianion 24, 2 equiv of carbon monoxide, and 1 equiv of phenyllithium in a process analogous to that required to form 27 would generate the trianion 28, the labeled analog of 22. Acylation of this substance with acetic anhydride, followed by loss of the oxygen originally present in 24, would in turn yield 26. Since the acetoxy group required to leave in this last step is activated toward heterolysis by two adjacent phenyl groups and one oxygen-substituted β-styryl moiety, sufficiently rapid conversion of 29 to 26 to preclude isolation of 29 would not be surprising; however, alternative schemes for conversion of 28 to 26 involving, e.g., monoaclylation of the oxygen derived from 27 followed by rapid loss of acetate ion, can of course also be written. We have no direct evidence for 29 or related species in these reactions, but the postulation of 28 as an intermediate is immediately compatible with the formation of compounds 1, 6, 7, and 8 as hydrolysis products from the reaction of phenyllithium and carbon monoxide by protonation, dehydration, and reverse aldol reactions, starting from the analogous trianion 22. The difference in the observed yields of 1 and 6 from

\[ \text{PhLi} + \text{CH}_2=\text{CHCl} \rightarrow \text{PhCHClCH}_2\text{Cl} \]

The reaction presumably reflects the sensitivity of 6 to the conditions encountered during the hydrolytic work-up.

Thus, examination of products derived from reactions of the labeled dithilium diaryl ketone dianion 24 with phenyllithium and carbon monoxide fully supports the hypothesis that dilithium benzophenone 18 is an intermediate in the reaction of phenyllithium and carbon monoxide and provides a unifying mechanistic rationalization for most of the products of this reaction based on conversion of 18 to intermediates having structures 17 and 22.

Oxidation of Dilithium Benzophenone and Lithium

Whitesides, et al. / Mechanism of Reaction of Carbon Monoxide with Phenyllithium
Benzophenone Ketyl by Carbon Monoxide. Benzpinacol (5) and benzil (3) are the sole isolated products of the reaction of phenyllithium and carbon monoxide not easily generated from 17 or 22. One possible rationalization for the formation of 5 rests on the demonstration that carbon monoxide is a sufficiently strong oxidizing agent to convert benzophenone dianion to benzophenone ketyl (and benzophenone ketyl ultimately to benzophenone). Carbon monoxide is an effective one-electron oxidant toward a variety of aromatic radical ions and dianions, toward metallic potassium, and toward solutions of potassium in ammonia, yielding in each case substances that can be derived from a hypothetical "alkali metal carbonyl" MO₂CO⁻.

Chemical and spectroscopic data demonstrate that carbon monoxide is also capable of oxidizing 18 and 19: the nature of the products derived from the carbon monoxide was not established in these experiments. Thus, Table 5 summarizes the yields of benzophenone and benzhydrol observed following hydrolysis of solutions of 18 and 19 that had been allowed to react to completion with carbon monoxide under conditions approximating those utilized for the reactions of carbon monoxide with phenyllithium. The observation of approximately equal yields of benzophenone and benzhydrol, characteristic of 19, after reaction and hydrolysis of either 18 or 19 with carbon monoxide in DME contrasts with the detection of benzophenone alone after reaction and hydrolysis of these substances in diethyl ether. The inference from these experiments is that carbon monoxide will oxidize 18 to 19 in either DME or ether but will oxidize 19 to benzophenone at a significant rate only in ether; this inference is in qualitative accord with the supposition that 19 should be less strongly reducing in the more strongly solvating DME than in the less basic ether.

Qualitatively similar conclusions were reached on examination of the changes induced in the visible spectra of solutions of 18 in ether and DME following exposure to carbon monoxide. In DME, this exposure results in disappearance of the band due to 18 and appearance of a band at 634 nm attributable to 19: in ether, addition of carbon monoxide results in complete bleaching, with the only new peak appearing at ~350 nm (benzophenone).

Reactions with Other Organometallic Reagents. We have examined briefly the reactivity of several other types of organometallic reagents toward carbon monoxide. These experiments, together with results obtained by others, indicate qualitatively that only derivatives of strongly basic anions will react with carbon monoxide under conditions similar to those used in the work described in this paper. Thus, tert-butyllithium, phenyllithium, n-butyl lithium, methyl-lithium, trimethylsilyllithium, and cyclopentadienyl-lithium readily absorb carbon monoxide, as do dimethylammonium and several lithium amides; the less basic lithium phenylacetylide, lithium n-butylacetylide, lithium diphenylamide, lithium cyclopentadienide, and lithium diphenylphosphide appear not to react. These data suggest that in classifying anions according to their reactivity toward carbon monoxide it may be heuristically valuable to consider these reactions as proceeding through acyl anions (30) whether or not substances of this class are true intermediates.

Values for pKₐ's of species containing the acyl anion moiety are not well-established, although that of CH₃CO⁻ (30, B = OCH₃) has been estimated to be ca. 35; this value seems consistent with what little is known about the chemistry of acyl anions. These organolithium reagents that have so far been found to react with carbon monoxide all are derivatives of anions having pKₐ's of this magnitude or greater, while those that have proved unreactive are characterized by pKₐ's that are smaller. Thus, it may prove possible to predict the facility of addition of organic anions to carbon monoxide on the basis of their basicity relative to that of the appropriate acyl anion 30.

Discussion

Three principal kinds of data bear on the mechanism of the reaction of phenyllithium with carbon monoxide. First, spectroscopic studies indicate that dilithium benzophenone dianion is formed in the early stages of the reaction. Second, examination of the products of reactions of carbon monoxide with a mixture of labeled

Table V. Yields of Benzophenone and Benzhydrol Obtained by Oxidation of Dilithium Benzophenone Dianion (18) and Lithium Benzophenone Ketyl (19) with Carbon Monoxide, Followed by Hydrolysisa

<table>
<thead>
<tr>
<th>Compound (concn, M)</th>
<th>Solvent</th>
<th>Product (% yield)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Ph₂CO</td>
</tr>
<tr>
<td>18 (0.06)</td>
<td>DME</td>
<td>50</td>
</tr>
<tr>
<td>18 (0.004)</td>
<td>Et₂O</td>
<td>20</td>
</tr>
<tr>
<td>19 (0.05)</td>
<td>DME</td>
<td>52</td>
</tr>
<tr>
<td>19 (0.003)</td>
<td>Et₂O</td>
<td>95</td>
</tr>
</tbody>
</table>

* Yields are based on the initial concentration of 18 or 19. The fate of the organic moieties not detected as benzophenone or benzhydrol in these experiments was not established.

(53) E. G. Kelly, Ph.D. Thesis, Massachusetts Institute of Technology, Cambridge, Mass., 1968. The major products from the reaction of n-butyllithium with carbon monoxide in hexane resemble those produced from phenyllithium, viz. dibutyl ketone (3-6%), 6-butylandecane-5,6-dione (10%).

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dilithium benzophenone dianion and phenyllithium establishes that the diarylmethylene moiety of the former is effectively incorporated into products characteristic of the reaction of carbon monoxide with phenyllithium. Third, examination of the influence of temperature and reaction composition on the distribution of products indicates that at least two related processes compete in these reaction mixtures: one, taking place at room temperature, converts 3 equiv of phenyllithium and 2 equiv of carbon monoxide to the lithium enolate of \( \alpha, \beta \)-diphenylacetophenone (17); a second, dominating at \(-78^\circ\), involves 3 equiv of phenyllithium and 3 equiv of carbon monoxide and generates the trilithium trianion 22. The products of the reaction isolated following quenching with water or acetic anhydride are derived in straightforward ways from 17 and 22. The mechanism implied by these data is summarized in Scheme III, together with speculations concerning the derivation of certain of the minor products and the structures of undetected intermediates between established structures.

Concerning the complexity of this mechanism, and of the resulting product mixtures, suggests that many of the various intermediates formed during the course of the reaction take part in further reactions with carbon monoxide and one another at rates that are comparable with or faster than the initial rate of formation of dilithium benzophenone dianion 18. In particular, our inability to generate more than traces (ca. 1\%\) of benzhydrox on hydrolysis of reactive mixtures that have absorbed only small quantities of carbon monoxide indicates that the concentration of 18 is never high and that its subsequent reactions with carbon monoxide and phenyllithium (or benzoyllithium, whichever is actually involved) are faster than its formation. Further, since the particular combinations of benzophenone dianion, carbon monoxide, and phenyllithium shown in Scheme III are certainly not the only ones that can be written, the low product yields observed under many conditions may result from condensations of these materials in different combinations to yield higher molecular weight products. The factors influencing the partitioning of intermediates between the reaction paths so far identified have not been established. One attempt to test the hypothesis that the relative importance of the low- and high-temperature paths for the reaction reflected the concentration of carbon monoxide in solution by studying the reaction at high carbon monoxide pressure was frustrated by a drop in the product balance; further studies have not been carried out.

The most important mechanistic question still unresolved concerning this reaction is the importance of benzoyllithium in these transformations. Qualitative correlation of the reactivity toward carbon monoxide of a number of organolithium reagents with their basicity is compatible with, but does not demand, production of transitory acyllithium compounds as the first intermediate in these reactions; the plausibility of these materials as intermediates is increased by previous work in which they have also been implicated. Nonetheless, there is no unambiguous method of distinguishing between, e.g., conversion of monomeric phenyllithium to dilithium benzophenone dianion 18 by way of benzoyllithium and conversion of dimeric phenyllithium to 18 by a concerted insertion of carbon monoxide into an aggregate; similarly, there is presently no way of deciding whether or not transformations of 18 to 22 or 17 involve benzoyllithium.

In a more general vein, the reaction of organic anions with carbon monoxide would seem to hold promise as a method of generating a number of unusual types of organic anions—especially dilithium dianions of symmetrical ketones and possibly acyllithium reagents—provided that ways can be devised to inhibit the condensation reactions that lead to formation of the mechanistically significant but synthetically unappealing types of products encountered in these studies.

**Experimental Section**

**General Methods.** Reactions involving organometallic reagents were carried out using standard techniques for manipulation of oxygen and water-sensitive compounds. Melting points were determined using a Thomas-Hoover capillary melting point apparatus and are uncorrected. Boiling points are uncorrected. Nmr spectra were run on Varian A-60 or Varian T-60 spectrometers; chemical shifts are reported in ppm downfield from TMS and coupling constants in Hz. Infared spectra were taken in sodium chloride cells using a Perkin-Elmer Model 237B grating spectrophotometer. Ultraviolet spectra were determined on a Cary 14

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spectrophotometer. Mass spectra were determined on a Hitachi-Perkin-Elmer RMU-6D or RMU-6E mass spectrometer. Glpc analyses were performed on a F & M Model 810 instruments equipped with flame ionization detectors and Disc integrators. Analytical thin-layer chromatography (tlc) was performed using Baker-flex precoated plates coated with silica gel 60F-254. Preparative plates were either analytical plates precoated using silica gel GF or home-made plates coated with Merck Silica gel PF-254. Diethyl ether was distilled from lithium aluminum hydride or calcium hydride under a nitrogen atmosphere immediately before use; 1,2-dimethyloxetane (DME), tetrahydrofuran (THF), and benzene were purified by distillation under nitrogen from an air-free atmosphere. Alcohols were distilled from sodium sulfate, passed through a solution of disodium benzophenone di-anion in DME, or taken directly from the cylinder without treatment. Glpc analyses for compounds 1 and 2 were carried out using an 8-ft column packed with 5% DEGS on Chromosorb W or a 2-ft column packed with 5% Carbosolve 20M on 80–100 mesh Chromospher P using n-alkanes as internal standards. Analyses of 3, 4, and 5 were carried out using a 2-ft column packed with 5% SE-30 on 80–100 mesh Chromospher P using eicosane as an internal standard. Analyses for 10, 11, 25, and 26 were carried out with either a 4-ft or 8-ft column packed with 3% OV-17 on 80–100 mesh Chromospher P using octadecane as internal standard. Phenyllithium, prepared using standard procedures; n-butyllithium in hexane was purchased from the Foote Mineral Corp. Concentrations of organolithium reagents were determined using a double titration method.17,18 Organolithium reagent solutions were discarded when the concentration of residual base in these analyses exceeded 10% of that organolithium reagent; however, residual base titration had no obvious influence on product distributions. Microanalyses were performed by Midwest Microabs, Inc.

1,3,3-Triphenyl-1-propene (16). Benzyltriphenylphosphonium chloride (4.3 g, 15 mmol) in 50 ml of ether was added to a dry, 200-ml, three-necked flask equipped with a condenser, dropping funnel, and nitrogen inlet tube. n-Butyllithium (10 ml, 1.5 N, 15 mmol) was added slowly to the vigorously stirred solution and the resulting orange mixture was allowed to stir for 25–30 min. To this solution was added 3.8 g (20 mmol) of 2,6-di-p-nitrophenylacetophenone in ether. The resulting mixture was allowed to reflux overnight, yielding an almost colorless solution and a white precipitate. The mixture was treated with 0.5 ml of concentrated hydrochloric acid. The resulting orange oil remaining was distilled through a short-path still to yield 1.1 g (3.7 mmol, 73%) of 7 as a yellow oil, bp 155–159°C (0.1 Torr).

The most convenient procedure for the preparation of 7 involved hydrolysis of 11, isolated from an acetic anhydride quench of the low temperature reaction of phenyllithium with carbon monoxide. Briefly, a solution of 11 (0.054 g, 0.25 mmol) in 15 ml of methanol was treated with 0.5 ml of concentrated hydrochloric acid. The solution was allowed to reflux for 4 hr and was then saturated with sodium chloride. The organic products were extracted with three 30-ml portions of ether. The combined ether phase was washed with aqueous sodium bicarbonate solution, water, and aqueous sodium chloride solution, dried (MgSO4), and concentrated to give 1.33 g of a crude yellow oil. Compound 7 was isolated in 60% yield from this oil by preparative tlc.

1,1,2-Triphenylethane-1,2-diol. a,a-Diphenyl-a-hydroxyacetoephone (0.078 g, 0.97 mmol) in 3 ml of ethyl ether was added slowly with stirring to a stirred solution of lithium aluminum hydride (0.138 g, 3.65 mmol) in 15 ml of ethyl ether under nitrogen at room temperature. After 15 min, the reaction was quenched by the slow addition of ethyl acetate. Several milliliters of ethyl ether was added, followed by several milliliters of water. The organic layer was separated and dried (Na2SO4). The solvent was removed, leaving a solid which was recrystallized from absolute ethanol giving 0.20 g (72%) of 1,1,2-triphenylethane-1,2-diol, having mp 165–166°C (lit.16 mp 165–166°C).

1,2,2-Triphenyl-1-acetoxyethane (10) was prepared from 2 by the method of House and Trost19 in 65% yield or in 52% yield by a procedure analogous to that described for 25 (except that LiTMP was used in place of lithium diisopropylamide): mp 104–105°C; nmr (CDCl3) 6 7.2 (m, 15), 1.85 (s, 3), and 1.83 (s, 3); ir (KBr) 3030, 2915, 1715, 1500, 1440, 1375, 1270, 1180, 1150, 1020, 980, 950, 880 cm-1; mass spectrum (70 eV) m/e (rel intensity) 314 (16, M+), 273 (22), 254, 235, 216, 197, 178, 159, 147, 135, 120, 110, 100, 92, 91, 80, 89, 88, 87, 86, 85, 84, 83, 82, 72, 71, 70, 69, 68, 67, 66, 65, 64, 63, 62, 61, 60, 59, 58, 57, 56, 55, 54, 53, 52, 51, 50, 49, 48, 47, 46, 45, 44, 43, 42, 41, 40, 39, 38, 37, 36, 35, 34, 33, 32, 31, 30, 29, 28, 27, 26, 25, 24, 23, 22, 21, 20, 19, 18, 17, 16, 15, 14, 13, 12, 11, 10, 9, 8, 7, 6, 5, 4, 3, 2, 1.

Anal. Calcd for C31H26O: C, 84.05; H, 5.77. Found: C, 83.98; H, 5.92.

1,3,3-Triphenyl-2-acetoxy-prop-2-en-3-one (11) was isolated as the major product on quenching the mixture obtained by reaction between phenyllithium and carbon monoxide at –70°C with acetic anhydride. An ether solution of 0.05 mmol of phenyllithium at –70°C until reaction was complete. Freshly distilled acetic anhydride (10.2 g, 100 mmol) was added by syringe to the vigorously stirring solution. The solvent was removed in vacuo under a nitrogen atmosphere. The orange oil remaining was distilled through a short-path still to yield 1.1 g (3.7 mmol, 73%) of 7 as a yellow oil, bp 155–159°C (0.1 Torr).

The most convenient procedure for the preparation of 7 involved hydrolysis of 11, isolated from an acetic anhydride quench of the low temperature reaction of phenyllithium with carbon monoxide. Briefly, a solution of 11 (0.054 g, 0.25 mmol) in 15 ml of methanol was treated with 0.5 ml of concentrated hydrochloric acid. The solution was allowed to reflux for 4 hr and was then saturated with sodium chloride. The organic products were extracted with three 30-ml portions of ether. The combined ether phase was washed with aqueous sodium bicarbonate solution, water, and aqueous sodium chloride solution, dried (MgSO4), and concentrated to give 1.33 g of a crude yellow oil. Compound 7 was isolated in 60% yield from this oil by preparative tlc.

1,1,2-Triphenylethane-1,2-diol. a,a-Diphenyl-a-hydroxyacetoephone (0.078 g, 0.97 mmol) in 3 ml of ethyl ether was added slowly to a stirred solution of lithium aluminum hydride (0.138 g, 3.65 mmol) in 15 ml of ethyl ether under nitrogen at room temperature. After 15 min, the reaction was quenched by the slow addition of ethyl acetate. Several milliliters of ethyl ether was added, followed by several milliliters of water. The organic layer was separated and dried (Na2SO4). The solvent was removed, leaving a solid which was recrystallized from absolute ethanol giving 0.20 g (72%) of 1,1,2-triphenylethane-1,2-diol, having mp 165–166°C (lit.16 mp 165–166°C).
method of Norton. Acetophenone (18 g, 0.15 mol), 17.4 ml of cyclohexylamine (15 g, 0.15 mol), and 10 ml of benzene were placed in a 50-ml round-bottomed flask equipped with a Dean-Stark trap, reflux condenser, Teflon-coated magnetic stirring bar, and outlet to a bubbler. The apparatus was swept with nitrogen and the reaction mixture refluxed for 6 hr. After continuous removal of water for 12 hr, the mixture was cooled down to 20°C and transferred by cannula to a flame-dried storage flask. Titration against 2-butanol, using 1.10-phenanthroline as an indicator, yielded a value of 0.67 M for the 105 ml of benzylmagnesium chloride solution for use in the procedure described below. Step 2. To a solution of 105 ml of 0.67 M benzylmagnesium chloride in ether (70 mmol) in a 250-ml, three-necked, round-bottomed flask equipped with a Teflon-coated magnetic stirring bar, a reflux condenser, and No-Air stoppers was added by cannula a solution of 20.6 g of 23 (70 mmol) in 100 ml of ether. Each drop of ketone was turned a deep purple as it struck the solution of Grignard reagent, the color fading with stirring. After addition was complete, the reaction mixture was stirred for 0.5 hr. The solution was then filtered by cannula to 50 ml of stirred ice water. To the resulting slurry was added 35 ml of cold 20% sulfuric acid. The organic layer was separated, the aqueous layer extracted with two 50-ml portions of ether, and the organic layers dried (MgSO$_4$), and concentrated under reduced pressure. The resulting residue was distilled in a 100 ml distillation flask, yielding 90 g of product (0.42 mmol, 56%).

1.1-Di(4-tert-butylphenyl)-2-phenylethanol (31) was synthesized by a procedure analogous to that described by Adkins and Zartman. To a solution of 105 ml of 0.67 M benzylmagnesium chloride in ether (70 mmol) in a 250-ml, three-necked, round-bottomed flask equipped with a Teflon-coated magnetic stirring bar, a reflux condenser, and No-Air stoppers was added by cannula a solution of 20.6 g of 23 (70 mmol) in 100 ml of ether. Each drop of ketone was turned a deep purple as it struck the solution of Grignard reagent, the color fading with stirring. After addition was complete, the reaction mixture was stirred for 0.5 hr. The solution was then filtered by cannula to 50 ml of stirred ice water. To the resulting slurry was added 35 ml of cold 20% sulfuric acid. The organic layer was separated, the aqueous layer extracted with two 50-ml portions of ether, and the organic layers dried (MgSO$_4$), and concentrated under reduced pressure. The resulting residue was distilled in a 100 ml distillation flask, yielding 90 g of product (0.42 mmol, 56%).

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ml of ether were placed in a flame-dried, 125-ml round-bottomed flask equipped with a Teflon-coated magnetic stirring bar and No-Air stopper. The flask was swept with nitrogen and cooled in an ice bath and 5.0 ml of a 1.6 M solution of methyllithium in ether was added by cannula. The mixture was then cooled to -60° for 1 hr; then 1.6 g (17.5 mmol) of 2,2-dimethylpropane-lithium in ether was added by cannula. Evolution of methane was evident during the addition. The mixture was stirred for 10 min, cooled to -78°, and a solution of 15.1 g (50 mmol) of 23 in 80 ml of THF was added by cannula. This yellow solution was stirred for 1 hr at 0° and 1 hr at 25° and was then quenched by addition to a stirred solution of 10 ml of acetic anhydride in 75 ml of ether. The resulting suspension was treated with 100 ml of saturated aqueous sodium bicarbonate solution and the organic layer was separated, dried (MgSO₄), and concentrated to give 3.5 g of white solid which was a mixture of benzaldehyde and 1,1-di(4-tert-butylphenyl)-2-acetoxy-3-phenyl prop-1-en-3-one. Diphenylketene[2] (9.7 g, 50 mmol) in 30 ml of ethyl ether was added slowly to a solution of 1,1-di-tert-butyl phenyl lithium (77.5 mmol) in 120 ml of ether at room temperature with vigorous stirring. After the addition was complete, the reaction mixture was held at reflux temperature for 30 min, cooled to 0°, and hydrolyzed with 20 ml of a saturated aqueous solution of ammonium chloride. The water (30 ml) was added and the ether layer was separated. The aqueous layer was extracted with two 100-ml portions of ether. The ether portions were combined, washed with water, and dried (CaCl₂). The ether was removed, leaving a solid which was dissolved in absolute ethanol, treated with decolorizing charcoal, and recrystallized from ethanol (10.5%) of white crystals: mp 102-103°; ir (CCl₄) 1690 cm⁻¹ (C=O); nmr (CCl₄) 6 1.13 (s, 9), 1.22 (t, 3, J = 8 Hz, CH₃). Anal. Calc. for C₉H₁₂O₂: C, 81.96; H, 6.72.

3,3-Dimethyl-1-phenyl-2-hydroxy-1-butanone (38). To a solution of 3 g (15 mmol) of 2-phenyl-1,3-dithiacyclohexane in 100 ml of dry tetrahydrofuran cooled to -60° was slowly added 10 ml (15 mmol, 1.5 N) of n-butyllithium. The solution was allowed to stir for 60° for 1 hr; then 30 ml (15 mmol) of 2,2,6,6-tetramethylpiperidine was slowly added and the solution was allowed to warm to -28° over a 4-hr period. The solution was hydrolyzed and the organic layer was separated and washed with aqueous sodium chloride solution, dried (Na₂SO₄), and concentrated to give 3.5 g of a mixture of the starting thiokeetal and another compound. Without further purification, the 3.5 g of white solid was added to a 500-ml, round-bottomed flask containing 200 ml of 91 methanol:water and 3.24 g (15 mmol) of mercuric oxide. The mixture was stirred at 0° for 1 hr; then 40 ml of freshly distilled THF were placed in a flame-dried, 300-ml, round-bottomed flask equipped with a Teflon-coated magnetic stirring bar and No-Air stopper. This mixture was swept with trap-to-trap at 1 Torr to remove the last traces of acetic anhydride and 2,2,6,6-tetramethylpiperidine. The orange solid remaining was recrystallized from ethanol to yield 0.75 g (57%) of 37: mp 168-169°; nmr (CCl₄) 6 1.13 (s, 9), 1.22 (t, 3, J = 8 Hz, CH₃). Anal. Calc. for C₉H₁₂O₂: C, 81.96; H, 6.72.

1,1-Di(4-tert-butylphenyl)-3-phenylprop-1-en-3-one (26). Freshly distilled THF (20 ml) and 2.2,6,6-tetramethylpiperidine (0.42 g, 3 mmol) were placed in a flame-dried 100-ml round-bottomed flask equipped with a Teflon-coated magnetic stirring bar and No-Air stopper. This solution was treated with decolorizing charcoal, and recrystallized from ethanol (26%) to yield 0.75 g (57%) of 37: mp 168-169°; nmr (CCl₄) 6 1.13 (s, 9), 1.22 (t, 3, J = 8 Hz, CH₃). Anal. Calc. for C₉H₁₂O₂: C, 81.96; H, 6.72.
chloride was separated by filtration and washed with small portions of methylene chloride and then was added to a mixture of 100 ml of water and 100 ml of benzene. The benzene layer was separated, washed with aqueous sodium chloride, dried (MgSO₄), and concentrated to give 0.9 g (37%) of 3,3-dimethyl-1,2-butanedione: mp 33-35°; νMax (CCl₄) 1728, 1638 cm⁻¹; nmr (CDCl₃) δ 7.25-7.9 (m, 5), 4.68 (d, 1, J = 8 Hz), 3.3 (d, 1, J = 8 Hz). 0.85 (s, 9).


Isolation and Characterization of Products by Glpc. Benzenophene and benzil were identified by comparison of glpc retention times, mass spectra, and infrared spectra of collected samples with those of authentic samples. Compounds 2 and 4 were isolated by combining several hydrolyzed reaction mixtures. The solvent was removed leaving a yellow oil which was dissolved in a minimum volume of methylene chloride. The resulting brown reaction mixture was quenched by the addition of 0.5 ml of distilled water. Saturated aqueous ammonium chloride solution (1 ml) and ether (15 ml) were added, and the ether layer was analyzed by glpc.

Isolation and Characterization of Products Using Preparative Thin-Layer Chromatography. Phenylbenzene and benzil were assayed by treating an aliquot of the original reaction mixture with saturated aqueous ammonium chloride solution and then subjected to preparative tlc. The solvent was an 8 : 2 : 1 benzene : ether : methylene dichloride mixture. The major unidentified spot had an Rf value of 0.49 on silica gel GF with 2 : 1 methylene chloride : cyclohexane eluent. This spot had characteristics on glpc using 2 : 1 methylene chloride : cyclohexane eluent. The ratio of the peak heights of the I10/I05 ions was 33 ± 0.6. Isotopic analyses of these samples showed that the ratio of peak heights of 18O/16O was 20 ± 0.6 and the ratio of peak heights of 12C/13C was 35 ± 0.5.


(77) An aliquot of phenyl-d₆-lithium was quenched with water; the resulting benzene, collected from an 8-ft 20% UC-W9 column and analyzed by mass-spectroscopy, was found to be 97.3% benzene-d₆, 2.7% benzene-d₅.

tions of water, dried (MgSO₄), and analyzed using a coupled gc-pc mass spectrometer.

Reaction of Phenyllithium and Carbon Monoxide in Ether and Treatment of the Resulting Reaction Mixture with Lithium Aluminum Hydride. A solution of 14 ml of 0.6 M phenyllithium (8.4 mmol) in ether and 25 ml of concentrated aqueous solution of sodium bicarbonate and dried (Na₂Sorb). The resulting suspension was washed with 100 ml of a saturated aqueous solution of sodium bicarbonate and dried (Na₂Sorb) and No-Air stopper was placed. 0.93 g of 23 (3.2 mmol) and 60 ml of freshly distilled ether. The reaction mixture was stirred overnight, during which time the solution had been reduced to benzhydrol.

Dilithium Benzophenone Dianion (18) from Benzophenone and Lithium. Benzophenone (23) (2.5 mmol), 40 ml of freshly distilled ether, and 0.1 g of lithium wire (14 mg-atoms) in an argon atmosphere. This mixture was analyzed by gcpc. Analysis of the gcpc data indicated that the benzophenone which had been added prior to treatment with LiAlH₄ had been reduced to benzhydrol.

Dilithium 4,4'-Di(tert-butyl)benzenophene Dianion (24). In a flame-dried, 100-ml round-bottomed flask equipped with a Teflon-coated magnetic stirring bar and a No-Air stopper was placed 0.93 g of 23 (3.2 mmol) and 60 ml of freshly distilled ether. The reaction mixture was analyzed by gcpc. Analysis of the gcpc data indicated that the benzophenone which had been added prior to treatment with LiAlH₄ had been reduced to benzhydrol.

Phenyllithium and Carbon Monoxide in the Presence of Carbon Monoxide. Ten milliliters of a 1-cm Pyrex spectrophotometer cell. Solutions of trityllithium and 17 were prepared and analyzed for stability with triphenylmethane and 10, respectively. Samples of dilithium benzophenone were prepared by addition of small amounts of 18 to 0.1 N solutions of phenyllithium contained in 1-cm Pyrex cells. Samples of 20 were prepared by reducing 74 mg of 1-phenyl-3,3'-dimethyl-1,2-butanediol (0.55 mmol) in 20 ml of DME and diluting aliquots of this stock solution approximately 1:2.5 with DME. Solutions of 15 were obtained by reaction of 1.1 equiv of LiTMP in ether, as described in the preparation of 26.

Samples used in studies involving the reaction of carbon monoxide with 18, 19, and 20 phenyllithium were carried out by mixing the reaction components directly in the spectrophotometer cell.

Dilithium 4,4'-Di(tert-butyl)benzenophene Dianion (24) in a flame-dried, 100-ml round-bottomed flask equipped with a Teflon-coated magnetic stirring bar and a No-Air stopper was placed 0.93 g of 23 (3.2 mmol) and 60 ml of freshly distilled ether. The reaction mixture was analyzed by gcpc. The gcpc data indicated that the benzophenone which had been added prior to treatment with LiAlH₄ had been reduced to benzhydrol.

Using a syringe, 20 ml of the red solution was withdrawn and added to a 50-ml erlenmeyer flask containing a Teflon-coated magnetic stirring bar. The solution was stirred in air until the red color had faded to pale green-yellow. This solution was treated with 20 ml of ether; the organic layer was separated, the aqueous layer was extracted once with 20 ml of ether, and the organic portions were combined, dried (MgSO₄), and analyzed by gcpc. Glpc analysis revealed the presence of 23 in 50% yield, with a small amount (ca. 10%) of the corresponding benzaldehyde as well as a small amount of a higher boiling material. The authentic sample of 23 was prepared by the reduction of 23 lithium aluminum hydride.

Using a syringe, another 20 ml of the red solution of 24 was withdrawn and added to a well-stirred solution of 10 ml of 2 N potassium hydroxide solution. After stirring for 10 min, the layers were separated, the aqueous layer was extracted with 20 ml of ether, the organic portions were combined, dried (MgSO₄), and analyzed by gcpc. Glpc analysis revealed only 4,4'-di(tert-butyl)-benzaldehyde as a product, with 88% yield.

Reaction of Phenyllithium with Carbon Monoxide in the Presence of Carbon Monoxide. In a typical experiment, a flame-dried, 100-ml round-bottomed flask equipped with a Teflon-coated magnetic stirring bar and a No-Air stopper was charged with 0.69 g of 4,4'-di(tert-butyl)-benzophenone (23) (2.5 mmol), 40 ml of freshly distilled ether, and 0.1 g of lithium wire (14 mg-atoms) in an argon atmosphere. This mixture was stirred overnight, during which time the solution turned a deep red. Into another flame-dried 100-ml round-bottomed flask equipped with a Teflon-coated magnetic stirring bar and a No-Air stopper was transferred by cannula 20 ml of a 1.25 N solution of phenyllithium in ether (25 mmol). To this solution was added by cannula the solution of 24 described above. This reaction mixture was stirred for 3 hr at 25° (or for 5 hr at ~78°) under an atmosphere of carbon monoxide. The reaction mixture was then transferred by cannula to a stirred solution of 20 ml of acetic anhydride in 75 ml of freshly distilled ether cooled in an ice bath. The resulting suspension was washed with 100 ml of a saturated aqueous solution of sodium bicarbonate and dried (Na₂Sorb). This solution was diluted to 300 ml with ether, dotriacetonotrCane was added as an internal standard, and the reaction mixture was analyzed by gcpc.

The Reaction of Dilithium Benzophenone Dianion with p-Ethylphenyllithium in the Presence of Carbon Monoxide. A mixture of dilithium benzophenone dianion (0.093 M, 1.3 mmol, 14.0 ml) in DME containing a known amount of n-nonadecane as an internal standard and p-ethylphenyllithium (0.08 N, 2.0 mmol) in ethyl ether was stirred under 1 atm pressure of carbon monoxide at room temperature for 2 hr. The reaction mixture was hydrolyzed with 0.2 ml of aqueous potassium hydroxide solution (pH 13), 5 ml of ether was added and the reaction mixture was analyzed by gcpc. a,a-Diphenyl-p-ethylphenyllithium was identified by comparison of its physical properties with those of an authentic sample.

The Reduction of a,a-Diphenyl-p-hydroxyacetophenone with
Dilithium Benzophenone Dianion. Butyllithium in hexane (6.0 mmol) was added slowly to 1,2-dibromoethane (0.957 g, 5.1 mmol) in a 40-ml centrifuge tube capped with a No-Air stopper. The resulting precipitate of anhydrous lithium bromide was washed four times with 20-ml portions of pentane, dissolved in 7 ml of hot DME, and added to 2 mmol of dipotassium benzophenone dianion in 30 ml of DME containing 0.1534 g of n-nonadecane as internal standard in a stoppered 40-ml centrifuge tube. The solution was thoroughly mixed by shaking and the precipitate of potassium bromide separated by centrifugation. The resulting solution of dilithium benzophenoned was added to a solution of α,α-diphenyl-α-hydroxyacetophenone (0.0967 g, 0.336 mmol) in 10 ml of DME. The red color of dilithium benzophenone persisted after the addition. After stirring at room temperature for 2 hr, the reaction mixture was hydrolyzed with aqueous potassium hydroxide solution; the aqueous layer was separated and extracted with one 50-ml portion of ethyl ether, and the organic layers were combined and dried (Na2SO4). Analysis by glpc indicated the presence of α,α-diphenylacetophenone (72%) and α,α-diphenyl-α-hydroxyacetophenone (9%).

Preparation of Other Anions. Lithium phenyl acetylide and lithium butyl acetylide were prepared by reaction of the corresponding acetylene with methyllithium in ether solution. Lithium diphenyl phosphide was prepared by the reaction of diphenylphosphine with n-butyllithium in THF. Lithium diphenylamide was prepared by the reaction of diphenylamine with methyllithium in THF. Sodium dimsylate was prepared as described by Greenwald, Chaykovsky, and Corey. All of the above were reacted with carbon monoxide at 200 psi; only sodium dimsylate took up an appreciable quantity of carbon monoxide (0.5 equiv of carbon monoxide per equivalent of dimsylate over a 24-hr period).

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(79) Solutions of 18 prepared using this procedure were analyzed for potassium by hydrolysis and treatment with lithium tetraphenylborate: cf. D. N. Bhattarcharyya, C. L. Lee, J. Smid, and M. Swarc, J. Phys. Chem., 69, 608 (1965). Less than 1% of the potassium originally present as dipotassium benzophenone remained in solution after addition of the lithium bromide.