Grants from the National Science Foundation for the purchase of a mass spectrometer and a Fourier transform NMR spectrometer.

(2) For a recent review, see H. O. House, *Acc. Chem. Res.*, **9**, 59 (1976).

(3) K. U. Ingold in "Free Radicals", Vol. 1, J. K. Kochi, Ed., Wiley-Interscience, New York, N.Y., 1973, pp 37–112; D. Lal, D. Griller, S. Husband, and K. U. Ingold, *J. Am. Chem. Soc.*, **96**, 6355 (1974).

(4) H. O. House and P. D. Weeks, *J. Am. Chem. Soc.*, **97**, 2778 (1975).

(5) (a) R. B. Bates, G. Büchi, T. Matsuura, and R. R. Schaffer, *J. Am. Chem. Soc.*, **82**, 2327 (1960); (b) R. E. Corbett and R. N. Speden, *J. Chem. Soc.*, 3710 (1958).

(6) J. A. Marshall and R. A. Ruden, *J. Org. Chem.*, **37**, 659 (1972).

(7) P. A. Grieco and R. Finkelhor, *J. Org. Chem.*, **38**, 2100 (1973).

(8) H. E. Zimmerman and C. J. Samuel, *J. Am. Chem. Soc.*, **97**, 4025 (1975).

(9) (a) H. O. House, W. L. Respess, and G. M. Whitesides, *J. Org. Chem.*, **31**, 3128 (1966); (b) L. D. Quin, J. W. Russell, Jr., R. D. Prince, and H. E. Shook, Jr., *ibid.*, **36**, 1495 (1971); (c) H. Hauth, D. Stauffacher, P. Niklaus, and A. Melera, *Helv. Chim. Acta*, **48**, 1087 (1965); (d) R. L. Clarke, S. J. Daum, P. E. Shaw, and R. K. Kullnig, *J. Am. Chem. Soc.*, **88**, 5865 (1966); (e) For a general discussion of this interaction, termed A^{1,3} strain, see F. Johnson, *Chem. Rev.*, **68**, 375 (1968).

(10) H. O. House, D. S. Crumrine, A. Y. Teranishi, and H. D. Olmstead, *J. Am. Chem. Soc.*, **95**, 3310 (1973).

(11) We found no evidence for a competing Michael reaction even when the solution containing the Li salt of the hydroxy ketone **24** was allowed to warm and dissociate.

(12) H. E. Simmons, T. L. Cairns, S. A. Vladuchick, and C. M. Hoiness, *Org. React.*, **20**, 1 (1973).

(13) W. S. Johnson and G. H. Daub, *Org. React.*, **6**, 39 (1951).

(14) H. O. House and P. D. Weeks, *J. Am. Chem. Soc.*, **97**, 2770 (1975).

(15) All melting points are corrected and all boiling points are uncorrected. Unless otherwise stated MgSO$_4$ was employed as a drying agent. The ir spectra were determined with a Perkin-Elmer Model 257 infrared recording spectrophotometer fitted with a grating. The uv spectra were determined with a Cary Model 14 or a Perkin-Elmer Model 202 recording spectrophotometer. The ^{1}H NMR spectra were determined at 60 MHz with a Varian Model A-60 or Model T-60-A NMR spectrometer and the ^{13}C NMR spectra were determined at 100 MHz with a JEOL Fourier transform spectrometer, Model PFT-100. The chemical shift values are expressed in δ values (ppm) relative to a Me$_4$Si internal standard. The mass spectra were obtained with an Hitachi (Perkin-Elmer) Model RMU-7 or a Varian Model M-6 mass spectrometer. All reactions involving strong bases or reactive organometallic intermediates were performed under either a nitrogen or an argon atmosphere.

(16) A mixture of the two isomeric olefins **17** and **22** has been described previously, bp 67 °C (0.5 mm), n^{20}D 1.4722: G. Sturtz, *Bull. Soc. Chim. Fr.*, 2349 (1964). We repeated this procedure, reaction of cyclohexanone with the sodium salt of *t*-BuCOCH$_2$P(O)(OEt)$_2$ in boiling DME, and found the product (46% yield) to be a mixture (NMR and GLC analyses) of ca. 70% of the olefin **22** and ca. 30% of the olefin **17**.

(17) Prepared by the procedure of R. S. Shank and H. Shechter, *J. Org. Chem.*, **24**, 1825 (1959). Also see R. D. Smith and H. E. Simmons, *Org. Synth.* **41**, 72 (1961), and ref 12.

(18) E. J. Corey and M. Chaykovsky, *J. Am. Chem. Soc.*, **84**, 867 (1962); **87**, 1353 (1965).

(19) (a) J. M. Conia, J. C. Limasset, and P. Amice, *Bull. Soc. Chim. Fr.*, 3981 (1969); (b) W. G. Dauben and G. H. Berezin, *J. Am. Chem. Soc.*, **85**, 486 (1963).

(20) J. W. Zubrick, B. I. Dunbar, and H. D. Durst, *Tetrahedron Lett.*, 71 (1975).

(21) (a) D. A. Evans, G. L. Carroll, and L. K. Truesdale, *J. Org. Chem.*, **39**, 914 (1974); (b) E. C. Evers, W. O. Freitag, J. N. Keith, W. A. Kriner, A. G. MacDiarmid, and S. Sujishi, *J. Am. Chem. Soc.*, **81**, 4493 (1959).

(22) In the reaction of the β-siloxy ketone **28** with KH, a catalytic amount of some alcohol was required in order to obtain reaction. If excess Me$_3$SiCN was present in the crude ketone **28** this reagent silylated the alcohol catalyst and no reaction occurred between the ketone **28** and KH.

(23) This band is more intense than the C═O band indicating that the enone **16** exists in a cisoid conformation **18a**. See (a) R. L. Erskine and E. S. Waight, *J. Chem. Soc.*, 3425 (1960); (b) A. J. Bowles, W. O. George, and W. F. Maddams, *J. Chem. Soc. B*, 810 (1969).

(24) H. C. Brown and G. W. Kabalka, *J. Am. Chem. Soc.*, **92**, 714 (1970).

(25) (a) H. O. House and E. F. Kinloch, *J. Org. Chem.*, **39**, 1173 (1974); (b) H. O. House, D. Koepsell, and W. Jaeger, *ibid.*, **38**, 1167 (1973); (c) K. W. Bowers, R. W. Giese, J. Grimshaw, H. O. House, N. H. Kolodny, K. Kronberger, and D. K. Roe, *J. Am. Chem. Soc.*, **92**, 2783 (1970).

(26) R. N. Adams, "Electrochemistry at Solid Electrodes", Marcel Dekker, New York, N.Y., 1969, pp 143–158.

Reactions Involving Electron Transfer. 11. Reaction of Lithium Dimethylcuprate with Diaryl Ketones[1]

Herbert O. House* and Chia-Yeh Chu

School of Chemistry, Georgia Institute of Technology, Atlanta, Georgia 30332

Received March 26, 1976

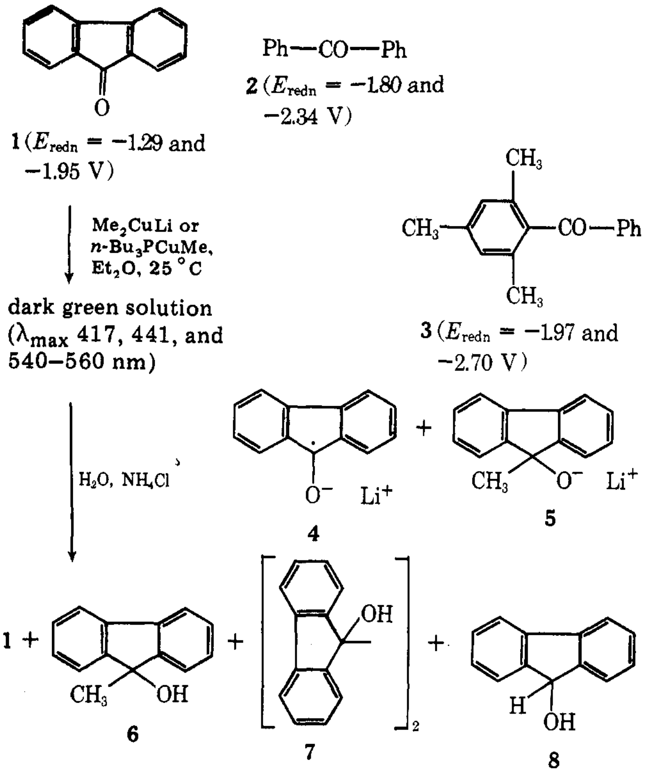
When cold, colorless solutions of PhCOPh and Me$_2$CuLi were mixed, an intermediate red-colored solution was formed. When this red solution, thought to arise from a charge-transfer absorption, was allowed to warm above 0 °C, a deep blue solution was formed and yellow (MeCu)$_n$ precipitated. This solution contained a mixture of the blue ketyl, Ph$_2\dot{C}$–O$^-$Li$^+$, and the salt of the 1,2 adduct **9**. When the more hindered diaryl ketone **3**, selected to retard 1,2 addition, was mixed with Me$_2$CuLi a yellow solution was formed that underwent no further change even at 25 °C. However, treatment of ketone **3** with a cold solution containing both Me$_2$CuLi and MeLi produced an initial yellow solution that turned red with precipitation of (MeCu)$_n$ as the solution was warmed above 0 °C. This red solution contained a mixture of the red ketyl **16** and the salt of the 1,2 adduct **14**. The observations with ketone **3** and mixtures of Me$_2$CuLi and MeLi suggest the formation of at least a small concentration of some more powerful reducing agent such as Me$_4$CuLi$_3$.

As noted in a recent paper,[2] it was of interest to examine the reactions of lithium dimethylcuprate (Me$_2$CuLi or Me$_4$Cu$_2$Li$_2$)[3] with alkyl aryl ketones (typical E_{redn} values −1.8 to −2.2 V) and with diaryl ketones (typical E_{redn} values −1.8 to −2.0 V) because the reduction potentials (E_{redn}) of these ketone substrates are sufficiently positive to permit[4] reactions with Me$_2$CuLi by a process involving an initial electron transfer step. Our study of reactions with alkyl aryl ketones is described elsewhere[2] and this paper describes our observations when the diaryl ketones **1–3** (Scheme I) were treated with Me$_2$CuLi.

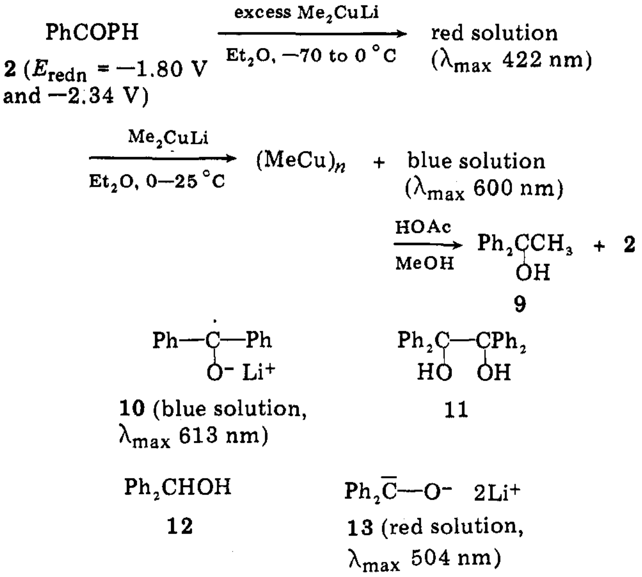
Some time ago we reported[5] that treatment of either Me$_2$CuLi or MeCuP(Bu-*n*)$_3$ with the very easily reduced[6] diaryl ketone **1** (Scheme I) formed immediately a deep green colored ethereal solution containing (EPR) a paramagnetic species. Hydrolysis of this solution yielded a mixture containing approximately equal amounts of the alcohol **6** and the diol **7** as well as minor amounts of the alcohol **8** and the starting ketone **1**. These observations indicate that the reaction of the ketone **1** with Me$_2$CuLi formed approximately equal amounts of the 1,2 adduct **5** and the ketyl **4**. This mixture, containing excess Me$_2$CuLi, underwent further change only very slowly.

Since reduction of the ketone **1** to the ketyl **4** occurs with unusual ease (E_{redn} = −1.29 V), we were concerned that the formation of the anion radical **4** in this case might not be indicative of the behavior with typical enones having E_{redn} values in the range −1.6 to −2.4 V. Consequently, we have examined the analogous reaction with benzophenone (**2**, E_{redn} = −1.80 and −2.34 V).[7] As summarized in Scheme II, mixing

Scheme I

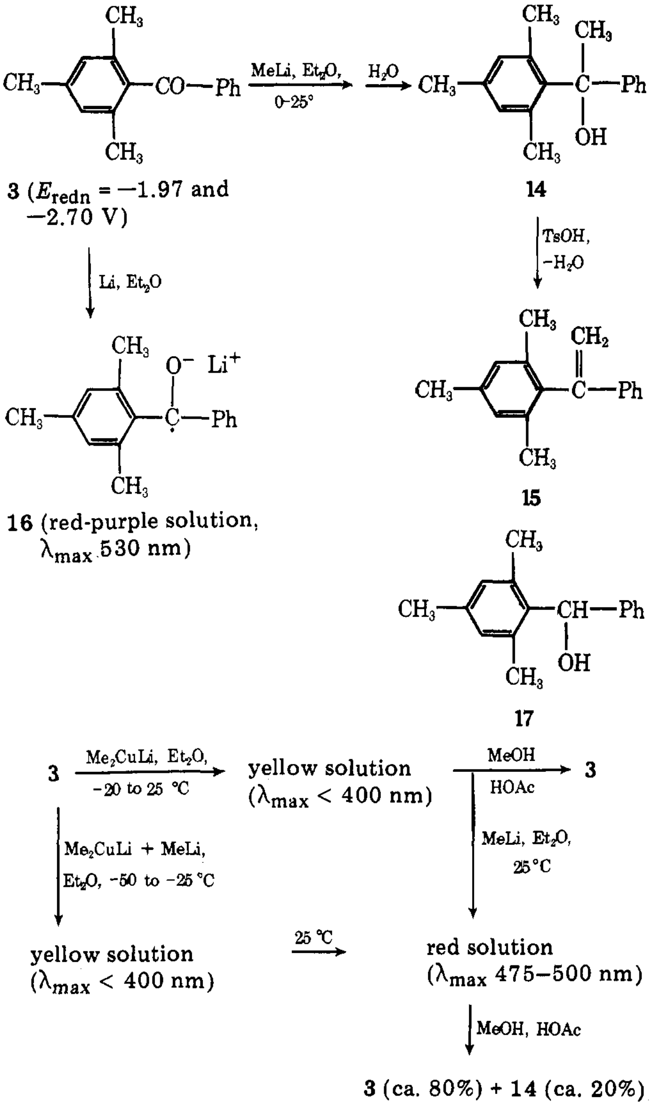


Scheme II



colorless solutions of PhCOPh and Me_2CuLi resulted in the immediate formation of a red solution. Although this red solution was stable for hours at low temperatures (−20 to −70 °C), when it was warmed to 0 °C, precipitation of yellow $(MeCu)_n$ began and the supernatant solution slowly changed from red to deep blue. The blue solution, containing excess Me_2CuLi and a yellow precipitate of $(MeCu)_n$, was stable for periods of at least 30 min at 25 °C. Examination of both the visible spectrum[8] and the EPR spectrum established that the blue species in the final solution was the lithium ketyl **10**. Quenching this solution yielded the alcohol **9** and the starting ketone **2** (formed by oxidation of ketyl **10** during the quenching process). The amounts of products **9** and **2** formed indicated that ca. 80% of the starting ketone **2** had been converted to the salt of the 1,2 adduct **9** and the remaining ketone **2** (ca. 20%) had been reduced to the ketyl **10**. Both of these changes had occurred during the period when the initially formed red solution was converted to a blue solution with precipitation of $(MeCu)_n$. Quenching the initial red solution yielded only unchanged ketone **2**. Although an ethereal solution of the dilithium salt **13** of benzophenone dianion is red (λ_{max} 504 nm), the visible absorption spectrum of **13** does not correspond to the spectrum of the red intermediate from benzophenone (**2**). Furthermore, quenching a solution of the dianion **13** yielded mainly alcohol **12** accompanied by lesser amounts of diol **11** and ketone **2** from oxidation during the quenching process. Consequently, the foregoing observations suggest that the initially formed red solution does not contain any substantial concentration of either the dianion **13** or any species in which a new carbon–carbon or carbon–metal bond has been formed. We have noted previously[9a] that a transient *red-to-orange* color has often been observed *before the precipitation of* $(MeCu)_n$ begins when phenyl-substituted enones are mixed with Me_2CuLi in ether solution. Thus, it seemed possible that this initially formed red species might be an intermediate in the formation of an anion radical (e.g., **10** from **2**) and/or an addition product (e.g., **9** from **2**).

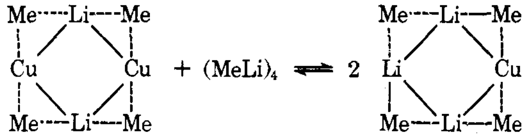
Scheme III



To explore further the possibility of observing a stepwise sequence of reactions with Me_2CuLi and diaryl ketones, we examined the reaction with the more hindered ketone **3** in the hope that we could retard or inhibit 1,2 addition. This ketone **3** is a member of a well-studied[10] family of 2,6-disubstituted phenyl ketones in which the steric bulk of the two ortho methyl groups causes the molecule to adopt a conformation with the 2,4,6-trisubstituted phenyl ring perpendicular to the plane of the carbonyl group. In this conformation, the two ortho methyl groups shield both sides of the carbonyl carbon atom. Mixing the ketone **3** (Scheme III) with an ethereal solution of MeLi (with or without LiBr) at −70 °C produced a yellow solution (λ_{max} <400 nm) from which the unchanged ketone **3** was recovered after quenching with a MeOH–HOAc mixture. When this yellow solution was warmed before quenching, above −10 °C the solution acquired a yellow-brown color (shoulder at ca. 500 nm) and subsequent quenching yielded the alcohol **14** also characterized as the olefin **15**.[11] Reaction of the ketone **3** with Li in Et_2O afforded a relatively stable red-to-purple solution of the ketyl **16** (λ_{max} 530 nm, intense EPR signal, $g = 2.0024$). On long standing, this red color slowly faded (presumably H^+ abstraction from the solvent); after hydrolysis the unchanged ketone **3** and the alcohol **17** were isolated.

When the ketone **3** was added to a solution of Me_2CuLi (containing no excess MeLi) at −20 °C, the resulting yellow solution exhibited no evidence (visible spectrum or EPR spectrum) for the formation of the ketyl **16**. Even when this solution was warmed to 25 °C, no visible absorption attributable to the ketyl **16** was observed and quenching the yellow solution afforded the unchanged ketone **3**. When the ketone **3** was added to a cold (−50 °C) solution of equimolar amounts of Me_2CuLi and MeLi, the resulting yellow solution exhibited no visible absorption attributable to the ketyl **16** and only a very weak EPR signal. However, as the solution was warmed above 0 °C, the solution deposited $(MeCu)_n$ and developed both an intense red color (λ_{max} 475–500 nm)[8] and an intense EPR signal ($g = 2.0020$) both attributable to the ketyl **16**. Quenching this red solution afforded a mixture of the alcohol **14** (ca. 20% of the product) and the ketone **3** (ca. 80% of the product). The various spectral changes and products observed in these reactions of either ketone **2** or **3** with a cuprate reagent were not significantly different when performed with solutions of cuprate reagents that either did or did not contain dissolved LiBr.[8]

These latter observations suggest that although neither Me_2CuLi nor MeLi in Et_2O solution is a sufficiently good reductant to reduce the ketone **3** to its ketyl **16**, some species formed when Et_2O solutions of Me_2CuLi and MeLi are mixed is capable of effecting this reduction. A recent report[12] of differing stereochemistry for the methyl carbinols formed by reaction of substituted cyclohexanones with MeLi and with a mixture of MeLi and Me_2CuLi could also be interpreted as evidence for the formation of this information would be the existence of equilibrium between the usual dimeric cuprate formulation **18** ($Me_4Cu_2Li_2$) and a small amount of a related organometallic cluster **19** having the composition Me_4CuLi_3. Such species are analogous to the mixed aggregate formed from MeLi and lithium halides.[13] If the species **19** (Me_4CuLi_3) is a more powerful reductant than $Me_4Cu_2Li_2$ (**18**) our observations with ketone **3** are readily explained.



18 **19**

However, the equilibrium concentration of an aggregate such as **19** appears to be small. In an earlier ¹H NMR study[5] when an Et_2O solution of MeLi and Me_2CuLi was cooled below −60 °C, the average ¹H NMR signal for the equilibrating methyl groups separated into two signals corresponding in position to the separate ¹H NMR signals for Me_2CuLi and MeLi but no signal was observed for a third species. We have now also examined the natural abundance ¹³C NMR spectra for solutions of MeLi, Me_2CuLi, and a mixture of the two. At room temperature an Et_2O solution of MeLi exhibited a single line at −13.4 ppm for the equilibrating methyl groups. As the solution was cooled below 0 °C this line began to broaden and at −40 °C appeared as a set of overlapping multiplets ($J_{^{13}C-^{7}Li} = 15$ Hz) corresponding to a ten-line multiplet (Me group bound to three equivalent ⁷Li atoms) and a seven-line multiplet (Me group bound to two ⁷Li atoms and one ⁶Li atom).[14] An Et_2O solution containing Me_2CuLi at 35 °C exhibited a single ¹³C NMR line at −9.6 ppm; this line remained narrow as the solution was cooled to −60 °C but did begin to broaden as the solution was further cooled to −80 °C. Unfortunately, the concentrated solution being used became so viscous at temperatures below −80 °C that we were unable to obtain satisfactory ¹³C NMR data at lower temperatures.

An Et_2O solution containing a mixture of MeLi and Me_2CuLi (average composition Me_4CuLi_3) at 35 °C exhibited a single ¹³C NMR peak (−11.1 ppm) corresponding to rapidly exchanging methyl groups. As the solution was cooled this peak broadened and at −40 °C appeared as two partially separated broad peaks at −9.0 and −13.1 ppm. Further cooling of these rather concentrated solutions to −60 °C resulted in precipitation of the MeLi and left a single narrow peak at −8.8 ppm corresponding to the solution of Me_2CuLi. Although this result was less definitive than the ¹H NMR data, we again observed no obvious signal attributable to a third organometallic species. Lack of solubility of the MeLi prevented us from obtaining meaningful measurements at lower temperatures.

To explore possible causes for the initial red color developed when PhCOPh (**2**) was mixed with Me_2CuLi (or the yellow color observed when ketone **3** was mixed with Me_2CuLi) we examined the ¹³C NMR spectra, the Raman spectra, and/or the visible spectra of solutions obtained by adding one of the ketones **2** or **3** to solutions of $LiClO_4$, to solutions of several Cu(II) compounds [$CuBr_2$, $Cu(OAc)_2$, $Cu(acac)_2$], and to solutions of the Cu(I) complex **20**.[15] We observed no evidence indicating the formation of complexes between the ketones **2** or **3** and any of the Cu(I) or Cu(II) compounds examined. Although we observed no new absorption in the Raman spectra or visible spectra of solutions prepared by adding one of the ketones **2**, **3**, **21**, or **22** to an Et_2O solution of $LiClO_4$, the ¹³C NMR spectra of these solutions did exhibit a small (3–6 ppm) downfield shift of the signals attributable to the carbonyl groups of each ketone. The ¹³C NMR signals for β-carbon atoms of the α,β-unsaturated ketones **21** and **22** were also shifted downfield 4–5 ppm when excess $LiClO_4$ was added to the Et_2O solutions. These observations suggest that in ethereal solvents, at least partial coordination of these ketones with Li^+ cation (e.g., structure **23**) does occur resulting in some reduction of the electron density at the carbonyl carbon atom and at the β-carbon atom of the enones **21** and **22**.

$(CH_3C{\equiv}N)_4Cu^+ClO_4^-$

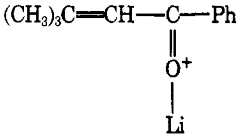
20

$(CH_3)_3C{=}CHCOPh$

21

$(CH_3)_3C{=}CHCOCH_3$

22



$$(CH_3)_3C{=}CH{-}\underset{\underset{\displaystyle Li}{|}}{\underset{O^+}{\overset{}{\underset{\|}{C}}}}{-}Ph$$

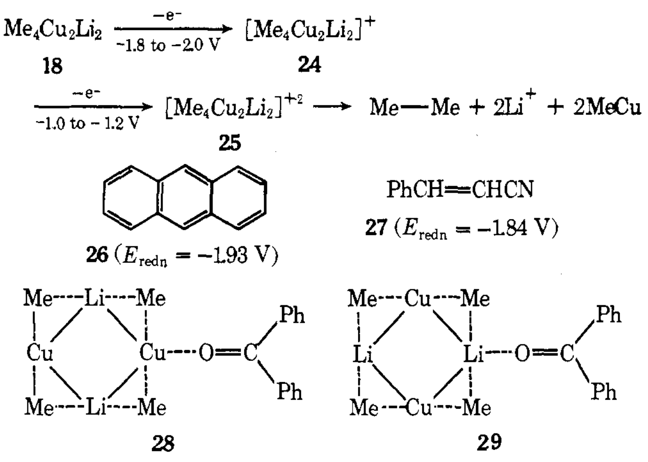
23

We used various spectrometric techniques to examine the colored solutions obtained immediately after adding one of the ketones **2** or **3** to a cold solution of Me_2CuLi. The EPR spectra of these solutions indicated that no appreciable concentration of one of the ketyls **10** or **16** was present. The Raman spectrum of the red solution from ketone **2** exhibited

C=C and C=O absorption that did not differ significantly from that observed for a solution of the ketone **2** in pure Et_2O. The ^1H and ^{13}C NMR spectra of these solutions were also very similar to the spectra of various separate components. In the ^{13}C NMR spectra of the colored solutions from ketones **2** and **3**, the signals attributable to the Me_2CuLi, the carbonyl carbon atom, and the aromatic para carbon atoms of the aryl rings were somewhat broader than the other NMR signals and the signals for the carbonyl carbon atoms were shifted to slightly (3–5 ppm) lower field. Thus, all of our data suggests that the species responsible for the red or yellow color in these initial solutions is present at low concentration and the bulk of the reactants, Me_2CuLi and ketone **2** or **3**, remain unchanged. All of this information is compatible with the idea that the initial colors observed in these solutions arise from charge-transfer absorption bands which need not bear any particular relationship to the subsequent reduction of the ketones **2** and **3** by cuprate reagents to form ketyls **10** and **16**.

Our previous observations,[4,9] indicating a relationship between the E_{redn} values for various unsaturated carbonyl compounds and their reaction with Me_2CuLi suggested that the oxidation of Me_2CuLi could be formulated as shown in Scheme IV. In an effort to measure directly the electrode potentials associated with the changes **18** → **24** → **25**, we have prepared solutions of Me_2CuLi in DME containing LiBr or $LiClO_4$ and in DMF containing n-Bu_4NBF_4 and examined their electrochemical behavior by cyclic voltammetry. In no case did we observe significant oxidation or reduction currents within the potential range −0.5 to −2.5 V. Analysis of these solutions by NMR established that Me_2CuLi was present and addition of anthracene (**26**) to a DMF solution of Me_2CuLi allowed us to obtain a typical cyclic voltammetry curve for this hydrocarbon **26**. Consequently, our failure to observe the electrochemical oxidation of **18** does not appear to be attributable either to decomposition of the cuprate or to a problem (e.g., electrode coating) with the electrochemical apparatus. In spite of these electrochemical results it is clear from the chemical reactions described that Me_2CuLi is capable of reducing both ketones **1** and **2** to the corresponding ketyls **4** and **10**. We believe that the most reasonable explanation of this apparent dilemma is to postulate that the transfer of an electron from the cuprate to a metal electrode surface is kinetically very slow. This postulate gains credibility when considered in light of the behavior of possible substrates **26** and **27** with Me_2CuLi. Although both the hydrocarbon **26** (E_{redn} = −1.93 V) and the nitrile **27** (E_{redn} = −1.84 V) are reduced at approximately the same potential as PhCOPh (E_{redn} = −1.80 V), both of these substrates **26** and **27** fail to react with an etheral solution of Me_2CuLi at 0–10 °C and are recovered unchanged. Because of these various observations, we are led to suggest that a necessary first step in the transfer of an electron from a cuprate to a substrate is the formation of a coordination complex such as **28** or **29**. Subsequent transfer of an electron could occur by a process analogous to an inner-sphere electron transfer mechanism in redox reactions of metal ions.

Scheme IV



$$\underset{18}{Me_4Cu_2Li_2} \xrightarrow[-1.8\text{ to }-2.0\text{ V}]{-e^-} \underset{24}{[Me_4Cu_2Li_2]^+} \xrightarrow[-1.0\text{ to }-1.2\text{ V}]{-e^-} \underset{25}{[Me_4Cu_2Li_2]^{+2}} \longrightarrow Me{-}Me + 2Li^+ + 2MeCu$$

26 (E_{redn} = −1.93 V)

PhCH=CHCN

27 (E_{redn} = −1.84 V)

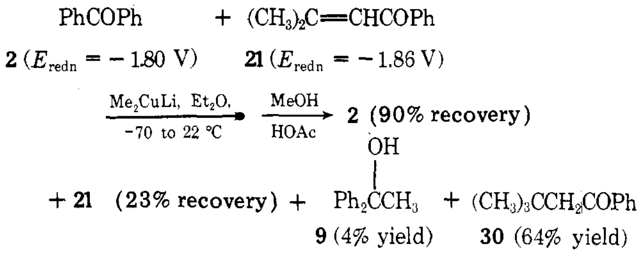
28

29

It is noteworthy that the substrates that are effective in abstracting an electron from cuprate reagents (carbonyl compounds, certain sulfones,[16] nitro compounds,[17] quinones,[17] O_2[17]) all contain a terminal oxygen atom that might be used to form complexes similar to **28** or **29**.

It was of interest to compare the rate of reaction of PhCOPh with Me_2CuLi to form the alcohol **9** with a typical conjugate addition of Me_2CuLi to an enone. For this comparison, we performed a competition experiment in which a limited amount (0.9 molar equiv) of Me_2CuLi was allowed to react with a mixture of 1 molar equiv of PhCOPh and 1 molar equiv of the enone **21** (Scheme V). This enone **21**, which has almost the same E_{redn} value as PhCOPh, is known[2] to react with Me_2CuLi to form the conjugate adduct **30**. Furthermore, when the enone **21** is mixed with a cold (−60 to −70 °C) solution of Me_2CuLi, a red solution is obtained immediately. As this solution is warmed, reaction occurs with precipitation of $(MeCu)_n$ and loss of the red color to give the adduct **30**. When this competition experiment was performed by mixing the reactants at −70 °C and then warming them until reaction occurred, the major materials isolated were the adduct **30** and the unchanged ketone **2** with lesser amounts of the enone **21** and only a small amount of the alcohol **9**. From these results, we conclude that reaction of Me_2CuLi with the enone **21** is *at least* 15 times as rapid as addition to PhCOPh. As a result of this experiment and related experiments with aryl alkyl ketones,[2] we conclude that 1,2 additions of Me_2CuLi both to diaryl ketones and to aryl alkyl ketones are significantly slower than conjugate additions of Me_2CuLi to enones.

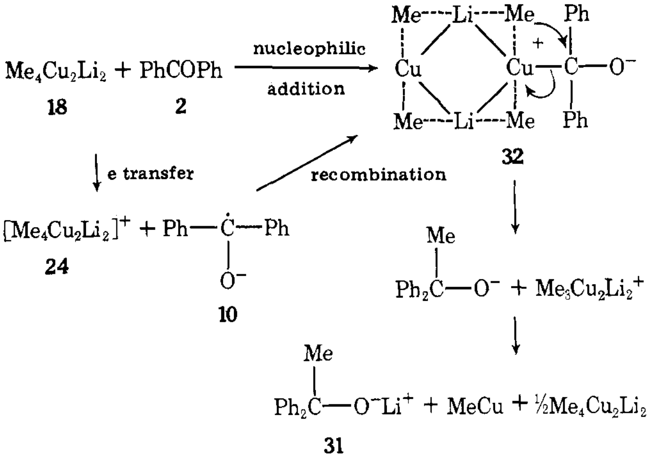
Scheme V



$$\underset{2\ (E_{redn} = -1.80\text{ V})}{PhCOPh} + \underset{21\ (E_{redn} = -1.86\text{ V})}{(CH_3)_2C{=}CHCOPh} \xrightarrow[-70\text{ to }22\ ^\circ\text{C}]{Me_2CuLi,\ Et_2O} \xrightarrow[HOAc]{MeOH} 2\ (90\%\ \text{recovery}) + 21\ (23\%\ \text{recovery}) + \underset{9\ (4\%\ \text{yield})}{Ph_2\overset{\overset{OH}{|}}{C}CH_3} + \underset{30\ (64\%\ \text{yield})}{(CH_3)_3CCH_2COPh}$$

The present studies provide even more compelling evidence than the related study of Me_2CuLi with aryl alkyl ketones[2] that Me_2CuLi does transfer an electron to an easily reducible ketone such as **2** (Scheme VI). The point of uncertainty in

Scheme VI



18 **2** **32** **24** **10** **31**

both studies is what relationship this electron-transfer process bears to the formation of a 1,2 adduct (e.g., **31** from **2**). Our data do not exclude a possible competing nucleophilic addition of the cuprate **18** to the ketone **2** to form an intermediate **32** that would be expected to yield the 1,2 adduct **31**. Of course the same intermediate **32** (leading to **31**) could be formed by recombination of the ion radical intermediates **10** and **24** produced by electron transfer. While our data do not unambiguously distinguish between these pathways to the 1,2 adduct **31**, it is appropriate to note that with both ketones **2** and **3** studied we have observed the formation of a 1,2 adduct only under reaction conditions where the corresponding ketyl (e.g., **10**) is also being generated. Thus, both the observations reported here and the related studies with aryl alkyl ketones[2] provide circumstantial evidence supporting the idea that the predominant reaction pathway in all of these reactions involves an initial electron-transfer step. In the present studies with diaryl ketones, it would appear that the recombination step **24** + **10** → **32** is particularly slow allowing a significant amount of the oxidized cuprate intermediate **24** to decompose before recombination can occur. As a result, appreciable concentrations of the ketyls such as **10** accumulate in the reaction mixture.

Experimental Section[18]

Preparation or Purification of Starting Materials. All ethereal solvents were freshly distilled from $LiAlH_4$, commercial Et_2O solutions of MeLi (halide free, Foote Mineral Co.) were standardized by a double titration procedure,[19] and the colorless, crystalline complex, Me_2SCuBr, was prepared from commercial CuBr (Fisher Scientific) as previously described.[9b] Ethereal solutions of MeLi containing an equimolar amount of LiBr were prepared from CH_3Br in the usual way.[20] A typical solution contained[19] 1.00 M MeLi. Previously described[21] procedures were also used to obtain pure DMF,[21] n-Bu_4NBF_4,[21] and $LiClO_4(DME)_2$.[7,22] Commercial "anhydrous" LiBr (City Chemical Corp.) was recrystallized repeatedly from DME (8.0 g of LiBr per 15 ml of DME) to give the complex, $LiBr(DME)_2$,[22] as white cubes. Commercial samples of the ketone **2**, mp 46–48 °C, and alcohols **12**, mp 65.5–66 °C, and **11**, mp 184–186 °C (dependent on rate of heating), were used (with purification[23] when necessary) and an authentic sample of the alcohol **9**, mp 80–81.5 °C, was available from previous work.[23,24] The ketone **3**, prepared by the acylation of mesitylene with PhCOCl and $AlCl_3$, was obtained in 94% yield as a colorless liquid: bp 195–197 °C (20 mm); $n^{25}D$ 1.5779 [lit. bp 120–122 °C (0.5 mm),[25a] 180–182 °C (11 mm)[25b]]; ir (CCl_4) 1672 cm^{-1} (C=O); NMR (CCl_4) δ 7.1–7.9 (5 H, m, aryl CH), 6.79 (2 H, s, aryl CH), 2.26 (3 H, s, aryl CH_3), and 2.00 (6 H, s, aryl CH_3); uv max (95% EtOH) 248 nm (ϵ 7500) and 285 (shoulder, 1200). Utilizing previously described[21,26] apparatus and procedures, the polarographic reduction of solutions of the ketone **3** (3–8×10^{-3} M) in DMF containing 0.5 M n-Bu_4NBF_4 was measured. The $E_{1/2}$ values observed were −1.97 V vs. SCE (n = 0.6, i_d = 22–57 μA) and −2.70 V vs. SCE (n = 0.6, i_d = 13–26 μA).[27] The preparation and characterization of ketones **21** and **30** are described elsewhere.[2]

To analyze mixtures of the ketone **2** and alcohols **9**, **11**, and **12**, we employed high-pressure liquid chromatography (HPLC) with a C-18 Corasil column and CH_3CN–H_2O (2:3 v/v) as a reverse-phase eluent. With this system and an eluent flow rate of 4 ml/min, the retention times of the components were **12**, 1.0 min; **9**, 1.3 min; **2**, 1.5 min; **11**, 4.8 min; and naphthalene (an internal standard), 1.9 min. Better resolution of the first three components eluted was obtained with an eluent flow rate of 1 ml/min where the retention times were **12**, 3.9 min; **9**, 4.9 min; **2**, 6.5 min; and naphthalene (an internal standard), 7.8 min. For quantitative analysis of the various mixtures, response factors for the uv detector (254 nm) were obtained with known mixtures of authentic samples. Mixtures containing compounds **2**, **9**, **11**, and **12** could also be analyzed by TLC and NMR analyses. With an alumina TLC coating and benzene as an eluent, the R_f values were **2**, 0.68; **9**, 0.54; **12**, 0.42; and **11**, 0.62. The NMR spectra (CCl_4) of all the components **2**, **9**, **11**, and **12** exhibited an aryl CH multiplet within the region δ 7.0–8.0; in addition the carbinol **9** exhibited singlets at δ 1.83 (CH_3) and 1.93 (OH), the carbinol **12** exhibited broad peaks at δ 5.68 (benzylic CH) and 2.04 (OH), and the diol **11** exhibited at broad peak at δ 3.2 (OH).

Reaction of PhCOPh (2) with Me_2CuLi. A. Product Studies. To a cold (0 °C) solution of Me_2CuLi, prepared from 1110 mg (5.4 mmol) of Me_2SCuBr and 10.8 mmol of MeLi in 10.2 ml of Et_2O, was added a solution of 900 mg (4.94 mmol) of ketone **2** in 3 ml of Et_2O. The resulting solution, which immediately turned dark red, was stirred at 0 °C for 10 min and then at 25 °C for 30 min. The solution remained red during the 10 min at 0 °C but changed progressively to green and then to a blue color with a yellow precipitate as the solution was warmed from 0 to 25 °C. The blue solution (containing a yellow precipitate) exhibited no further change during a 60-min period at 25 °C. Then 8 ml of MeOH–HOAc (1:1 v/v, N_2 passed through the solution to remove dissolved O_2) was added, and the mixture was partitioned between Et_2O and an aqueous solution (pH 8) of NH_3 and NH_4Cl. The Et_2O layer was washed with aqueous $NaHCO_3$, dried, and concentrated to leave 846 mg of crude product as a yellow liquid that contained (HPLC with added naphthalene as an internal standard and NMR analysis) the ketone **2** (17% recovery) and the carbinol **9** (70% yield); neither the alcohol **12** nor the diol **11** was detected (HPLC analysis) in the crude product.

In a comparable reaction a solution (at 25 °C) of 5.4 mmol of Me_2CuLi in 10.2 ml of Et_2O was treated with a solution of 400 mg (2.2 mmol) of PhCOPh in 3.0 ml of Et_2O and the resulting mixture was stirred at 25 °C for 20 min. During this reaction period the initial reaction mixture was a deep red solution that turned green as a yellow precipitate began to separate. Within 5 min, the separation of the yellow precipitate was complete leaving a deep blue colored supernatant liquid. After the reaction mixture had been partitioned between Et_2O and water, the crude neutral organic product was isolated as 390 mg of yellow liquid containing (HPLC and NMR analysis) the ketone **2** (22% recovery) and the carbinol **9** (63% yield). The same procedure was repeated with 5.4 mmol of Me_2CuLi and 900 mg (4.94 mmol) of the ketone **2** in 13.2 ml of Et_2O to give 890 mg of crude liquid product containing (TLC, HPLC, and NMR analysis) the ketone **2** (26% recovery) and the alcohol **9** (53% yield). A portion of the crude product was chromatographed on alumina to separate 121 mg of early fractions (eluted with PhH) containing (TLC and NMR analysis) ketone **2**, 162 mg of intermediate fractions (mixtures of **2** and **9**, eluted with PhH), and 109 mg of fractions (eluted with PhH and PhH–Et_2O) containing (TLC and NMR analysis) the carbinol **9**. Recrystallization of the early fractions from Et_2O–hexane separated 86 mg of pure PhCOPh, mp 46–48 °C, and recrystallization of the late fractions from PhH separated 64 mg of the carbinol **9**, mp 80–81 °C.

To explore the effect of LiBr on this reaction, a previously described[28] procedure was used to obtain a solution of Me_2CuLi that did not contain an equimolar amount of a lithium halide. Reaction of 2.2 ml of an Et_2O solution containing 1.54 mmol of MeLi with a solution of 310 mg (1.50 mmol) of Me_2SCuBr in 2 ml of Et_2O and 2 ml of Me_2S yielded a yellow precipitate of $(MeCu)_n$ which was separated by centrifugation, washed with 2 ml of Et_2O, and then treated with 2.0 ml of an Et_2O solution containing 1.4 mmol of MeLi to give a colorless solution of halide-free Me_2CuLi. After this solution of Me_2CuLi had been cooled to 0 °C, it was treated with a solution of 220 mg (1.21 mmol) of PhCOPh in 2 ml of Et_2O. The resulting red solution was warmed from 0 to 25 °C during 20 min (during which time a yellow precipitate separated and the solution turned blue) and then quenched with 4 ml of a MeOH–HOAc mixture (deoxygenated with N_2). After the usual isolation procedure, analysis (HPLC with added internal standard) of the crude product (211 mg of colorless liquid) indicated the presence of the alcohol **9** (39% yield) and the ketone **2** (53% recovery).

In another experiment, a cold (−20 °C) solution of 2.14 mmol of Me_2CuLi in 8 ml of Et_2O was treated with a solution of 350 mg (1.92 mmol) of PhCOPh in 3 ml of Et_2O and the resulting solution was stirred at −20 °C for 20 min. After this solution had been quenched with 5 ml of MeOH–HOAc (1:1 v/v, flushed with N_2 to remove O_2), it was partitioned between Et_2O and an aqueous solution of NH_3 and NH_4Cl. The ethereal solution was washed with aqueous NaCl, dried, and concentrated to leave 327 mg of colorless liquid that contained (HPLC and NMR analyses) the starting ketone **2** (93% recovery) but none of the alcohols **9**, **11**, or **12**.

B. Studies of the Visible and EPR Spectra. To obtain authentic samples of the dianion **13** and the ketyl **10**, the following procedures were employed.[29]

A solution of the dianion **13** was obtained by stirring a solution of 1.276 g (7.0 mmol) of PhCOPh in 30 ml of Et_2O with 0.4 g (56 mg-atoms) of Li wire at 25 °C for 18 h. The solution initially turned a blue color corresponding to the ketyl **10** and then slowly became dark red in color as the dianion **13** formed. The solution was quenched with 5 ml of MeOH–HOAc (1:1 v/v, flushed with N_2 to remove O_2) and subjected to the usual isolation procedure to separate 1.28 mg of crude neutral product containing (HPLC and NMR analysis) ketone **2** (22% recovery) and alcohols **12** (30% yield) and **11** (47% yield). A portion of the same solution of dianion **13** was diluted with Et_2O containing 0.3 mmol of MeLi (a scavenger for O_2 and protic impurities) and then exhibited a visible absorption maximum at 504 nm with an absorbance of 0.71 corresponding to ϵ 2100 if conversion of **2** to the dianion **13** (maximum concentration 3.39×10^{-4} M) was complete. When excess ethereal Me_2CuLi was added to this solution, the principal maximum (at 504 nm) remained with a new shoulder at ca. 590 nm. When an ethereal solution of the dianion **13** was deliberately oxidized by adding O_2 (air) to the cell, the solution changed from red to blue in color with loss of the absorption maximum at 504 nm and the appearance of a new maximum at 614 nm corresponding to the ketyl **10**. Further oxidation gave a colorless solution of PhCOPh. The reported[29] maximum for an Et_2O solution of the dianion **13** is 494 nm (ϵ 25 000).

A solution of the ketyl **10** was obtained[29] by treating 96 mg (0.26 mmol) of the pinacol **11** in 25 ml of Et_2O with 1.2 ml of an Et_2O solution containing 1.15 mmol of MeLi. After the resulting blue solution had been stirred at 25 °C for 20 min, it was quenched with 10 ml of MeOH-HOAc (1:1 v/v, flushed with N_2 to remove O_2) and subjected to the usual isolation procedure to separate 98 mg of crude neutral product as a yellow liquid containing (TLC, HPLC, and NMR analysis) the ketone **2** (ca. 44%) and the alcohols **12** (ca. 3%) and **11** (ca. 53%). A comparable solution of the ketyl **10** from 96 mg (0.26 mmol) of the pinacol **11** and 1.2 mmol of MeLi (halide free) in 1.2 ml of Et_2O exhibited a maximum at 613 nm with an absorbance of 0.71 corresponding to ϵ 213 if all of the pinacol **11** was converted to ketyl **10**. The reported[29] absorption maximum for an Et_2O solution of the ketyl **10** is 600 nm (whether the MeLi used contained LiBr was not stated).[8] When the ketyl **10** was prepared from diol **11** and MeLi containing LiBr, the absorption maximum was 598 nm. An analogous blue solution of the ketyl **10**, prepared from 7.3 mg (0.02 mmol) of the diol **11**, and 1.0 mmol of MeLi (halide free) in 11 ml of Et_2O exhibited an intense EPR signal[30] with $g = 2.0028$. In certain of the preparations of this ketyl **10**, partial resolution of the hyperfine structure was achieved.[31]

When the Et_2O solution of PhCOPh was added to a cold (−20 °C) ethereal solution of excess 0.2 M Me_2CuLi (from halide-free MeLi and Me_2SCuBr) in a uv cell and the resulting red solution was scanned rapidly, a broad peak was observed at 422 nm. As the solution warmed, with corresponding color changes from red to yellow to green to blue, the peak at 422 nm was gradually replaced by a new maximum at 600–610 nm corresponding to the ketyl **10**. When 1 equiv of PhCOPh was added to an Et_2O solution of Me_2CuLi at 25 °C, the initial scan of the resulting blue solution exhibited a maximum at 600 nm corresponding to the ketyl **10**. Similarly, as a cold (−78 °C) red solution, prepared from 45 mg (0.22 mmol) of Me_2SCuBr, 0.4 mmol of MeLi, 40 mg (0.2 mmol) of ketone **2**, and 2 ml of Et_2O exhibited a weak EPR signal ($g = 2.0027$)[30] that increased in intensity substantially as the solution was warmed to 25 °C and became blue in color.

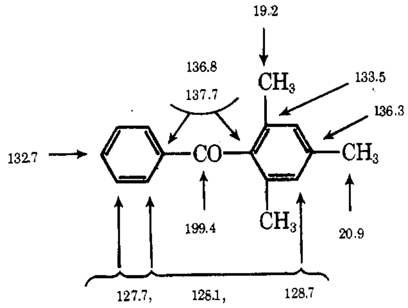
Reactions of Ketone 3. A. With MeLi. To a cold (0 °C) solution of 1.80 g (8.04 mmol) of the ketone **3** in 10 ml of Et_2O was added, dropwise and with stirring, 15 ml of an Et_2O solution containing 10.5 mmol of halide-free MeLi. The resulting yellowish-brown solution was stirred at 25 °C for 25 min and then partitioned between Et_2O and H_2O. After the organic layer had been dried and concentrated, the crude product, 1.86 g of yellow liquid, contained [ir, NMR, and TLC analysis, silica gel with Et_2O-pentane (1:9 v/v) as eluent] mainly the alcohol **14** (R_f 0.28) accompanied by a small amount of the starting ketone **3** (R_f 0.48). Chromatography on silica gel with an Et_2O-pentane eluent (1:24 v/v) separated 1.563 g (81%) of the liquid alcohol **14**. A portion of the product was distilled in a short-path still to separate the alcohol **14** as a pale yellow liquid: bp 145–147 °C (1.1 mm); $n^{25}\mathrm{D}$ 1.5776; ir (CCl_4) 3595 cm^{-1} (OH); uv (95% EtOH) a series of weak maxima (ϵ 393 or less) in the region 245–260 nm; NMR (CCl_4) δ 7.0–7.4 (5 H, m, phenyl CH), 6.68 (2 H, s, aryl CH), 2.18 (3 H, s, aryl CH_3), 2.10 (6 H, s, aryl CH_3), 1.88 (3 H, s, CH_3CO), and 1.68 (1 H, s, OH, exchanged with D_2O); mass spectrum *m/e* (rel intensity) 240 (M^+, <1), 223 (13), 222 (58), 208 (18), 207 (100), 206 (18), 192 (45), 191 (12), and 96 (11).

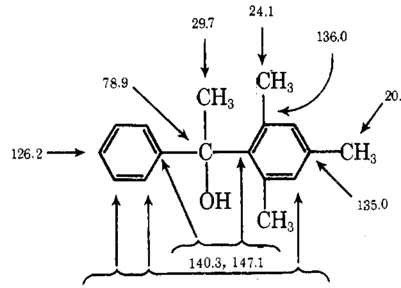
Anal. Calcd for $C_{17}H_{20}O$: C, 84.95; H, 8.39. Found: C, 84.98; H, 8.40.

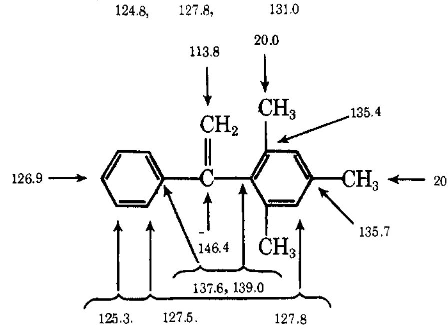
In another experiment, a solution of 168 mg (0.75 mmol) of the ketone **3** in 5 ml of Et_2O was maintained at −70 °C during the addition of 1.2 ml of an Et_2O solution containing 0.84 mmol of halide-free MeLi. The resulting yellow-colored solution was stirred at −70 °C for 1 h and then quenched with a cold mixture of MeOH and HOAc (5:1 v/v) and subjected to the usual isolation procedure. The crude liquid product (167 mg) contained (ir and NMR analyses) the starting ketone **3** and no alcohol **14** was detected. A comparable experiment was performed by preparing a cold (−70 °C) solution of 1.0 mmol of ketone **3** and 2.0 mmol of MeLi (containing LiBr) in 10 ml of Et_2O. This pale yellow solution, which exhibited no significant absorbtion above 400 nm, was allowed to warm slowly. At ca. −10 °C the solution became yellowish-brown in color and exhibited intense absorption below 450 nm with a shoulder at ca. 500 nm. Thus, the color and absorption of the reaction solution from ketone **3** and MeLi are comparable in the presence or in the absence of LiBr.

Mixtures of the alcohol **14** and the ketone **3** could also be analyzed by GLC (Carbowax 20M on Chromosorb P), the products elected being the olefin **15** (retention time 2.4 min, from dehydration of the alcohol **14**) and the ketone **3** (5.2 min). A sample of the olefin **15**, collected (GLC) after injection of the alcohol **14**, was obtained as a colorless liquid, $n^{25}\mathrm{D}$ 1.5833, that was identified with the subsequently described sample by comparison of GLC retention times and NMR spectra. After a solution of 377 mg (1.57 mmol) of the alcohol **14** and 50 mg of $p\text{-}CH_3C_6H_4SO_3H$ in 25 ml of PhH had refluxed for 30 min, the solution was washed with aqueous $NaHCO_3$, dried, and concentrated. Distillation of the residual liquid in a short-path still separated 247 mg (71%) of the olefin **15** as a pale yellow liquid: bp 122–125 °C (0.7 mm); $n^{25}\mathrm{D}$ 1.5830 [lit.[11] bp 120 °C (3 mm), $n^{20}\mathrm{D}$ 1.5835]; ir (CCl_4) 1613 (C=C) and 905 cm^{-1} ($C{=}CH_2$); uv max (95% EtOH) 247 nm (ϵ 6500); NMR (CCl_4) δ 7.1–7.4 (5 H, m, phenyl CH), 6.81 (2 H, s, aryl CH), 5.92 (1 H, d, J = 1.5 Hz, vinyl CH), 5.04 (1 H, d, J = 1.5 Hz, vinyl CH), 2.27 (3 H, s, aryl CH_3), and 2.07 (6 H, s, aryl CH_3); mass spectrum *m/e* (rel intensity) 222 (M^+, 48), 208 (20), 207 (100), 206 (20), 192 (58), and 41 (19).

The natural abundance ^{13}C NMR spectra ($CDCl_3$ solution) of the ketone **3**, the alcohol **14**, and the olefin **15** are summarized in the following formulas. The assignments are compatible with relative peak areas and with off-resonance decoupling measurements.







B. With Me_2CuLi. To 10 ml of a solution (at 25 °C) of 5.0 mmol of Me_2CuLi was added, dropwise with stirring, 684 mg (3.0 mmol) of the ketone **3**. The resulting yellow solution was stirred at 25 °C for 30 min. A comparable yellow solution exhibited broad absorption at 380–400 nm with no resolved absorption peak at longer wavelength. When excess ethereal MeLi was added to this yellow solution, the solution developed a red color and exhibited a new absorption maximum within the range 510–525 nm. After the yellow reaction solution had been subjected to the usual isolation procedure, the crude liquid product contained (GLC and NMR analysis) the starting ketone **3** but no alcohol **14** was detected. In a comparable experiment where the solution of Me_2CuLi and ketone **3** was stirred at 25 °C for 18 h, the crude product isolated again contained (GLC) only the starting ketone **3**.

A comparable yellow solution was obtained by adding 45 mg (0.2 mmol) of the ketone **3** in 1 ml of Et_2O to a cold (−50 °C) solution of Me_2CuLi, from 205 mg (1.0 mmol) of Me_2SCuBr, 1.8 mmol of MeLi (containing LiBr), and 11.8 ml of Et_2O. At −20 °C this solution exhibited no EPR signal.[30] After the solution had been warmed to 25 °C during 40 min, the resulting yellow solution exhibited a very weak EPR signal, $g = 2.0020$, corresponding to the subsequently described ketyl **16**.

C. With the Reagent from Me_2CuLi and MeLi. To a solution (at 25 °C), prepared from 411 mg (2.0 mmol) of Me_2SCuBr, 6.0 mmol of MeLi, and 10 ml of Et_2O, was added a solution of 400 mg (1.79 mmol) of the ketone **3** and 2 ml of Et_2O. The resulting dark red solution was stirred at 25 °C for 30 min and then quenched with MeOH–HOAc (1:1 v/v, flushed with N_2) and subjected to the usual isolation procedure. The crude liquid product contained (NMR and GLC analyses) ca. 20% of the alcohol **14** and ca. 80% of the ketone **3**. Collected (GLC) samples of the ketone **3** and the olefin **15** (from dehydration of alcohol **14** in the GLC apparatus) were identified with previously described samples by comparison of GLC retention times and NMR and mass spectra.

When 23 mg (0.10 mmol) of ketone **3** was added to a cold (−50 °C) solution, from 0.49 mmol of Me_2CuBr, 1.4 mmol of MeLi (containing LiBr), and 10 ml of Et_2O, a yellow solution was obtained that remained yellow and exhibited no absorption maximum at longer wavelength than 400 nm as the solution was warmed to −20 °C. As the solution was further warmed to 25 °C, a red color developed and a new maximum appeared at ca. 475 nm. In a similar experiment where the ketone **3** was added to a solution (at 25 °C) of the reagent, Me_2CuLi + MeLi prepared with halide-free MeLi, the red solution exhibited a maximum at ca. 500 nm corresponding more closely to the absorption observed for the subsequently described ketyl **16** in the absence of LiBr.[8]

Similarly when a cold (−50 °C) solution, from 1.0 mmol of Me_2SCuBr, 2.9 mmol of MeLi (containing LiBr), 0.11 mmol of ketone **3**, and 11 ml of Et_2O, was examined at −20 °C, it exhibited an EPR signal[30] of only moderate intensity corresponding to the ketyl **16**. When the solution was warmed to 25 °C, the intensity of the EPR signal (at $g = 2.0020$) attributable to the ketyl **16** increased approximately 100-fold.

D. With Li. A solution of 700 mg (3.12 mmol) of the ketone **3** in 35 ml of Et_2O was stirred with 260 mg (37.1 mg-atoms) of Li wire under an argon atmosphere for 6 h at which time the gradually increasing absorbance of the red-purple solution had become constant. The solution of the ketyl **16** exhibited a maximum at 530 nm; the absorbance value corresponded to ϵ 930 if conversion of the ketone **3** to the ketyl **16** were complete. A comparable solution of the ketyl **16** exhibited a strong EPR signal, $g = 2.0024$,[30] with partial resolution of hyperfine structure.[32]

After a comparable red solution, from 700 mg (3.12 mmol) of the ketone **3** and 260 mg (37.1 mg-atoms) of Li in 35 ml of Et_2O, had been stirred for 10 days, the red color had faded to leave a yellow solution. This solution was quenched with MeOH–HOAc (1:1 v/v, flushed with N_2) and subjected to the usual isolation procedure. The crude liquid product (682 mg) contained (ir and NMR analysis) a mixture of the ketone **3** (ca. 20%) and the alocohol **17** (ca. 80%). Chromatography on silica gel with Et_2O–hexane (1:24 v/v) separated 367 mg of the alcohol **17** as a pale yellow liquid: $n^{25}D$ 1.5819 [lit. bp 138–139 °C (0.5 mm)[33a]]; ir (CCl_4) 3610 cm^{-1} (OH); NMR (CCl_4) δ 7.1–7.3 (5 H, m, phenyl CH), 6.74 (2 H, s, aryl CH), 6.17 (1 H, s, carbinol CH), 2.21 (3 H, s, aryl CH_3), 2.12 (6 H, s, aryl CH_3), and 2.04 (1H, broad, OH); uv (95% EtOH) shoulder at 216 nm (ϵ 17 300) with a series of weak maxima (ϵ 400 or less) in the region 257–274 nm;[33b] mass spectrum *m/e* (rel intensity) 226 (M^+, 30), 208 (30), 207 (25), 193 (100), 178 (28), 149 (39), 147 (47), 121 (47), 105 (98), 91 (41), 79 (38), 77 (85), and 51 (28).

Competitive Reaction of Me_2CuLi with Ketones 2 and 21. A solution of Me_2CuLi, from 925 mg (4.5 mmol) of Me_2SCuBr, 9.0 mmol of MeLi, and 8.6 ml of Et_2O, was cooled to −72 °C and a solution of 910 mg (5.0 mmol) of PhCOPh and 800 mg (5.0 mmol) of ketone **21** in 4.0 ml of Et_2O was added, dropwise and with stirring while the temperature was maintained at −65 to −72 °C. After the resulting red solution had been stirred for 5 min at −70 °C, it was allowed to warm slowly with stirring. At ca. −40 °C separation of $(MeCu)_n$ from the red solution began and when the solution had warmed to −20 °C, the solution was pale yellow with a copious precipitate of $(MeCu)_n$. The resulting mixture was warmed to 22 °C (with no further change in appearance) and then quenched with a MeOH–HOAc mixture and then filtered and partitioned between Et_2O and H_2O. The ethereal layer was washed with an aqueous solution (pH 8) of NH_3 and NH_4Cl and then dried and concentrated to leave 1.74 g of crude product as a pale yellow liquid. An aliquot of the crude product was mixed with naphthalene (an internal standard for HPLC analysis, C-18 Corasil column with CH_3CN–H_2O, 1:3 v/v, as eluent). The product contained (ir, NMR, and LC analyses) the carbinol **9** (retention time 3.3 min, ca. 4% yield), the ketone **21** (3.8 min, 23% recovery), the ketone **2** (4.8 min, 90% recovery), naphthalene (6.5 min), and the ketone **30** (64% yield).

Reaction of Me_2CuLi with Cinnamonitrile (27). To a cold (0 °C) solution of Me_2CuLi, from 1110 mg (5.4 mmol) of Me_2SCuBr, 10.8 mmol of MeLi, 5.0 ml of Me_2S, and 10.2 ml of Et_2O, was added a solution of 568 mg (4.4 mmol) of the nitrile **27** in 2 ml of Et_2O. After the yellow-orange solution had been stirred at 0 °C for 20 min, a 3.0-ml aliquot was removed and partitioned between H_2O and Et_2O. The crude neutral product obtained from the Et_2O solution amounted to 109 mg of yellow liquid with NMR absorption corresponding to the starting nitrile **27**.[34] The remainder of the reaction solution was stirred at 25 °C for 1 h and then subjected to the same isolation product. The crude product, 669 mg of red viscous liquid, was chromatographed on silica gel with Et_2O–hexane mixture as eluents. Early fractions eluted with Et_2O–hexane (1:4 v/v) provided 195 mg of crude product that contained (NMR analysis) mainly the starting nitrile **27**. Later chromatographic fractions exhibited broad, ill-defined NMR absorption and appeared to be a mixture of polymeric materials that contained no product from conjugate addition.

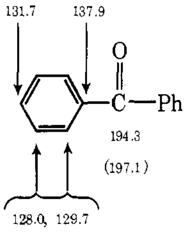
Earlier studies in our laboratory by Dr. Michael J. Umen had indicated that ethereal solutions of Me_2CuLi did not react with anthracene (**26**). To examine the behavior of this hydrocarbon **26** with a mixed reagent, a solution with the average composition Me_4CuLi_3 was prepared from 411 mg (2.0 mmol) of Me_2SCuBr and 8.0 mmol of halide-free MeLi in 4.5 ml of Et_2O. This solution was treated with a solution of 267 mg (1.5 mmol) of anthracene (**26**) in 5 ml of PhH and the resulting solution was stirred at 25 °C for 1 h and then subjected to the usual isolation procedure. The crude organic product (192 mg of colorless solid) had NMR absorption corresponding to unchanged anthracene (**26**). Analysis by GLC (Carbowax 20M on Chromosorb P) indicated the presence of anthracene (**26**, retention time 10.0 min) and no peak was observed corresponding to 9-methylanthracene (16.0 min).

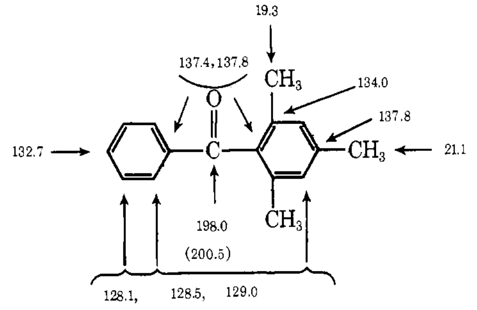
Preparation of the Complex 20. Following a previously described[15] procedure, a mixture of 572 mg (4.0 mmol) of Cu_2O, 1.31 g (32 mmol) of CH_3CN, 4.6 ml of aqueous 70% $HClO_4$ (32 mmol), and 25 ml of H_2O was refluxed under a N_2 atmosphere for 10 min and then allowed to cool. Colorless crystals of the complex **20** that separated were recrystallized from an H_2O–CH_3CN mixture to separate 851 mg (37%) of the complex **20** as colorless prisms. A CH_3CN solution of the complex **20** exhibited end absorption with ϵ 11 000 at 231 nm. Addition of either ketone **2** or ketone **3** to this solution produced no visible color and the uv spectrum of the mixtures showed only absorption bands attributable to the complex **20** and the added ketone **2** or **3**.

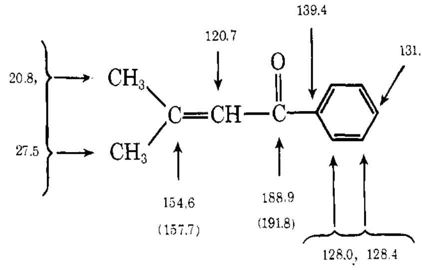
A series of experiments were performed in which solutions containing 0.01–0.5 molar equiv of various Cu(II) salts (with added solubilizing ligands) were mixed with 1.0 molar equiv of Ph_2CO. The Cu salts examined included $BrCuSMe_2$ in $CDCl_3$, $CuBr_2$ in DME and in CH_3CN, $Cu(OAc)_2$ in $CDCl_3$, and $Cu(acac)_2$ in $CDCl_3$. In all cases we observed no color change indicating an interaction between Ph_2CO and the Cu(II) compound. Also, even in the presence of substantial concentrations of the paramagnetic Cu(II) compounds, the ^{13}C NMR signals for Ph_2CO did not exhibit a substantial shifting or broadening; only the ^{13}C NMR signals for various added ligands or solvents were broadened. Thus, we found no evidence for significant association between these Cu(II) compounds and Ph_2CO.

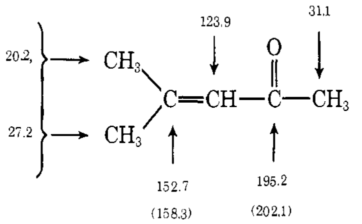
Raman Spectra of Reactants.[35] The Raman spectrum of an Et_2O solution of PhCOPh exhibited peaks at 1669 (C=O) and 1604 cm^{-1} (phenyl) with the region 1430–1510 cm^{-1} being obscured by absorption of the solvent, Et_2O.[36] The Raman spectrum of a solution of 45 mg (0.25 mmol) of the ketone **2** and 28 mg (0.26 mmol) of $LiClO_4$ in 0.50 ml of Et_2O exhibited comparable peaks at 1668 and 1603 cm^{-1}. Similarly, a solution of 36 mg (0.16 mmol) of ketone **3** in 0.70 ml of Et_2O exhibited Raman peaks at 1682 (C=O) and 1603 cm^{-1} (phenyl ring) and a solution of 230 mg (1.03 mmol) of ketone **3** and 230 mg (2.2 mmol) of $LiClO_4$ in 1.0 ml of Et_2O exhibited comparable peaks at 1681 and 1603 cm^{-1}. The Raman spectrum of a cold (−40 °C) red solution obtained from addition of PhCOPh to an Et_2O solution of Me_2CuLi exhibited bands at 1671 and 1604 cm^{-1} suggesting that the concentration of the species responsible for the red color is small.

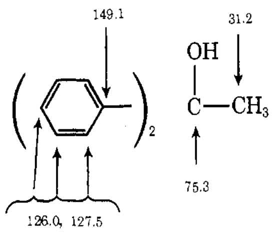
NMR Studies. A. Reactants. The subsequently described natural abundance of ^{13}C NMR spectra were measured in Et_2O with added C_6D_6 (ca. 20% by volume to provide a "lock" signal) and Me_4Si as an internal standard; the ^{13}C NMR lines arising from these solvents were found at 15.4 and 65.7 ppm (Et_2O signals) and at 126.6, 127.5, and 128.5 ppm (C_6D_6 signals). The assignments indicated are consistent with relative peak intensities and with off-resonance decoupling measurements. The ^{13}C NMR data for ketones **2**, **3**, **21**, and **22** were also measured in a solution containing 1.0–1.5 molar equiv of anhydrous $LiClO_4$. For those ^{13}C NMR signals that exhibited an appreciable shift (more than 1 ppm), the values in the presence of added $LiClO_4$ are indicated in parentheses. It will be noted that added $LiClO_4$ causes an appreciable downfield shift in the ^{13}C NMR signal for only the carbonyl carbon atom of the diaryl ketones **2** and **3** whereas both the carbonyl carbon atoms and the β-carbon atoms of the enones **21** and **22** undergo an appreciable downfield shift in signal.











A 1.6 M solution of halide-free MeLi in 1.5 mol of Et_2O containing 0.2 ml of C_6D_6 and 0.2 ml of Me_4Si exhibited a single ^{13}C NMR line for the MeLi at −13.4 ppm when measured at 35 °C. As the solution was cooled to 0 °C, this line broadened (half-band width 60 Hz). Upon further cooling to −40 °C, this line appeared as a multiplet centered at −13.2 ppm. This multiplet appeared to consist of a more intense ten-line pattern (eight of the ten lines were clearly resolved, $J_{^{13}C-^{7}Li} = 15$ Hz) expected[14] for a Me group bound to three equivalent ^7Li atoms. Superimposed upon this ten-line multiplet was a less intense seven-line multiplet ($J_{^{13}C-^{7}Li} = 15$ Hz), the pattern expected for approximately 20% of the Me groups that are bound to a tetrahedral face defined by two ^7Li atoms and one ^6Li atom. A solution of Me_2CuLi, prepared from 4 ml of an Et_2O solution containing 7.08 mmol of halide-free MeLi, 728 mg (3.64 mmol) of $BrCuSMe_2$, 0.3 ml of C_6D_6, and 0.2 ml of Me_4Si, exhibited a single ^{13}C NMR line for the Me groups at −9.6 ppm when measured at 35 °C. As the solution was cooled to −60 °C the half-band widths for the Me signals of Me_4Si and Me_2CuLi remained the same. Upon further cooling to −80 °C, the Me signal for Me_2CuLi (at −8.4 ppm) had a half-band width of 10 Hz while the half-band width for the Me_4Si signal was 5 Hz. Upon further cooling, the solutions became sufficiently viscous that all of the lines in the spectrum were seriously broadened.

A solution corresponding in stoichiometry to the composition Me_4CuLi_3 was prepared from 411 mg (2.0 mmol) of Me_2SCuBr, 4.5 ml of an Et_2O solution containing 8.0 mmol of halide-free MeLi, 0.2 ml of C_6D_6, and 0.1 ml of Me_4Si. As had been observed previously[5] in the ^1H NMR spectrum, the ^{13}C NMR spectrum of this solution at 35 °C exhibited a single peak at −11.1 ppm corresponding to the average signal for all of the methyl groups present in the organometallic reagent. As this solution was cooled, the peak broadened and at −40 °C had separated into two broad partially resolved peaks at −9.0 and −13.1 ppm. Further cooling to −60 °C was accompanied by precipitation of the MeLi to leave a single sharp signal at −8.8 ppm corresponding to the Me_2CuLi that remained in solution. These observations are compatible with the earlier ^1H NMR observations[5] where the signal at −78 Hz for the rapidly equilibrating Me groups separated into two signals at −72 and −112 Hz when the solution was cooled to −62.5 °C. As noted in earlier work,[5] the ^1H NMR signals for solutions (at 35 °C) of MeLi and Me_2CuLi were found as singlets at −110.5 and −57 Hz (half-band width 2.5 Hz) and the addition of extra MeLi to the Me_2CuLi solution moved the position of the ^1H NMR singlet (−57 Hz) to higher field. The ^1H and ^{13}C NMR signals for the Me_2S present in the Me_2CuLi solutions (prepared from Me_2SCuBr) were located at δ 2.00 and 17.8 ppm, respectively. A solution of MeLi in a mixture of Et_2O and DME containing excess $LiClO_4$ exhibited an ^1H NMR MeLi signal at −124 Hz. A comparable solution of Me_2CuLi in Et_2O and DME containing excess $LiClO_4$ exhibited an ^1H NMR signal at −99 Hz.

B. Reaction of PhCOPh with Me_2CuLi. A cold (ca. −60 °C) solution of Me_2CuLi, from 0.22 mmol of Me_2SCuBr and ca. 0.5 mmol of MeLi in 0.4 ml of Et_2O, containing Me_4Si was treated with 1 molar equiv of PhCOPh; the resulting red solution exhibited an ^1H NMR CH_3 singlet at −62 Hz with a half-band width of 2.5 Hz. When a second molar equiv of PhCOPh was added to the cold, red solution, the Me signal was shifted to −51.5 Hz. The remainder of the spectrum of this cold red solution exhibited peaks attributable to Et_2O, Me_2S, and PhCOPh but none of the alcohol product **9** was detected.

When a cold (−20 °C) solution of 3.0 mmol of Me_2CuLi in 3.3 ml of Et_2O containing 0.2 ml of C_6D_6 and 0.2 ml of Me_4Si was treated with 558 mg (3.0 mmol) of PhCOPh, the resulting red solution exhibited ^{13}C NMR signals attributable to Me_2CuLi and to PhCOPh at −9.3, 127.6, 128.5, 130.9, 135.8, and 199.6 ppm. In this spectrum, the signals at −9.3 (cuprate Me signals), 130.9 (*p*-C atoms of PhCOPh), and 199.6 ppm (C=O) were significantly broader than the other signals in the spectrum. This experiment was repeated with a cold (−30 to −40 °C) solution prepared from 250 mg (1.37 mmol) of PhCOPh and 1.46 mmol of the previously described *halide-free* Me_2CuLi in 1.0 ml of Et_2O. The ^{13}C NMR values observed, −9.6, 128.5, 130.7, 132.6, 136.3, and 198.9 ppm, were comparable to those observed in a reaction solution containing LiBr.

A solution prepared from 500 mg (2.75 mmol) of PhCOPh, 10 mg (0.027 mmol) of the diol **11**, 0.2 ml of C_6D_6, 0.3 ml of Me_4Si, and 1.0 ml of Et_2O was treated with 0.4 ml of an Et_2O solution containing 0.28 mmol of MeLi. The ^{13}C NMR spectrum of the resulting blue solution (containing PhCOPh and less than 0.02 molar equiv of the ketyl **10**) exhibited only peaks attributable to the solvents (Et_2O, C_6D_6, and Me_4Si). When the solution was exposed to air to oxidize the ketyl **10**, the blue color was discharged and the ^{13}C NMR spectrum then exhibited all of the additional peaks from the dissolved ketone **2**.

C. Reaction of Ketone 3 with Me_2CuLi. A cold (−20 °C) solution containing 3.0 mmol of Me_2CuLi, 0.2 ml of C_6D_6, and 0.2 ml of Me_4Si in 3.3 ml of Et_2O was treated with 672 mg (3.0 mmol) of the ketone **3**. The resulting yellow solution exhibited the following ^{13}C NMR signals attributable to the ketone **3** and Me_2CuLi: −9.6, 19.4, 21.2, 128.2, 129.2, 129.9, 133.4, 135.1, 135.7, 138.6, and 203.4 ppm. The signals at −9.6 (cuprate Me groups), 129.9, 135.1, and 203.4 ppm (C=O) were broadened when compared with the remaining signals in the spectrum. In a comparable experiment, a cold (0 °C) solution prepared from **3** and *halide-free* Me_2CuLi exhibited a carbonyl ^{13}C NMR signal at 202.3 ppm.

A solution of 500 mg (2.3 mmol) of the ketone **3** in 1 ml of Et_2O containing C_6D_6 and Me_4Si was stirred with 100 mg of Li wire until a red solution (a mixture of ketone **3** and ketyl **16**) was obtained. The ^{13}C NMR spectrum of the mixture exhibited broadened peaks attributable to C_6D_6, Et_2O, and Me_4Si, but no signals attributable to the ketone **3** were observed.

Electrochemical Measurements. Cyclic voltammetry measurements utilized previously described[7,21b] procedures, cells, and electrodes. A series of attempts were made to measure directly by cyclic voltammetry the electrode potential associated with the oxidation of Me_2CuLi, employing previously described combinations of either a bare Pt or Hg-coated Pt working electrode with a saturated calomel reference electrode fitted with appropriate salt bridges and a Pt wire as the counter electrode. For solvents and supporting electrolytes the combinations examined were 0.5 M *n*-Bu_4NBF_4 in DMF, 0.4 M LiBr in DME, and 0.5 M $LiClO_4$ in DME. Before use, the solutions of LiBr and $LiClO_4$ in DME were treated with small amounts of ethereal MeLi (as a scavenger for O_2 and protic impurities) and then centrifuged. Aliquots of ethereal Me_2CuLi (ca. 1 M) were added to these solvent–electrolyte systems and the resulting solutions were scanned by cyclic voltammetry from −0.5 V to −2.5 V vs. SCE. In no case were any oxidative or reductive current peaks observed that could be attributed to Me_2CuLi. In two cases ($LiClO_4$–DME–Et_2O and *n*-BuN_4BF_4–DMF–Et_2O) portions of the solutions were examined by ^{1}H NMR spectra to establish that the CH_3 peak attributable to Me_2CuLi was still present in these solutions being examined electrochemically. Since we have found that anthracene (**26**, $E_{1/2} = -1.93$ and -2.48 V vs. SCE)[21b] does not react with ethereal Me_2CuLi at 25 °C, it was possible to perform another control experiment. A solution of Me_2CuLi, from 0.30 g (1.5 mmol) of Me_2SCuBr and 2.9 mmol of MeLi in 2 ml of Et_2O, was mixed with 3 ml of DMF containing 0.5 M *n*-Bu_4NBF_4. Although this solution, whose ^{1}H NMR spectrum established that Me_2CuLi was still present in the DMF solution, exhibited no oxidative or reductive peak in the region −0.5 to −2.5 V, when anthracene was added to the solution a cyclic voltammetry scan characteristic[21b] of the reversible reduction of anthracene to its radical anion was readily observed.

Registry No.—**2**, 119-61-9; **3**, 954-16-5; **9**, 599-67-7; **14**, 59671-58-8; **15**, 1667-02-3; **16**, 59671-59-9; **17**, 21945-75-5; **20**, 14057-91-1; **21**, 5650-07-7; **27**, 4360-47-8; Me_2CuLi, 15681-48-8; MeLi, 917-54-4.

References and Notes

(1) This research has been supported by Public Health Service Grant 9-RO1-GM-20197 from the National Institute of General Medical Sciences. The execution of this research was also assisted by Institutional Research Grants from the National Science Foundation for the purchase of a mass spectrometer and a Fourier transform NMR spectrometer.

(2) H. O. House, A. V. Prabhu, J. M. Wilkins, and L. F. Lee, *J. Org. Chem.*, accompanying paper in this issue.

(3) Although several lines of evidence, summarized in ref 4, suggest that this reagent has a dimeric structure ($Me_4Cu_2Li_2$), analogous to $(MeLi)_4$, both for convenience and in accord with current practice [G. H. Posner, *Org. React.*, **19**, 1 (1972); **22**, 253 (1975)] we will continue to refer to this reagent as a monomer (Me_2CuLi) unless the nature of the discussion requires use of the dimeric formulation for clarity.

(4) For a recent summary, see H. O. House, *Acc. Chem. Res.*, **9**, 59 (1976).

(5) H. O. House, W. L. Respess, and G. M. Whitesides, *J. Org. Chem.*, **31**, 3128 (1966).

(6) H. O. House, L. E. Huber, and M. J. Umen, *J. Am. Chem. Soc.*, **94**, 8471 (1972).

(7) H. O. House and P. D. Weeks, *J. Am. Chem. Soc.*, **97**, 2785 (1975).

(8) The visible absorption maxima of Et_2O solutions of both ketyls **10** and **16** were shifted to shorter wavelengths when LiBr was present in the solutions. This phenomenon has been noted and discussed previously by P. G. Powell and E. Warhurst, *Trans. Faraday Soc.*, **58**, 953 (1962).

(9) (a) H. O. House and M. J. Umen, *J. Org. Chem.*, **38**, 3893 (1973); (b) H. O. House, C. Y. Chu, J. M. Wilkins, and M. J. Umen, *ibid.*, **40**, 1460 (1975).

(10) (a) M. S. Newman in "Steric Effects in Organic Chemistry", M. S. Newman, Ed., Wiley, New York, N.Y., 1956, pp 240–242; (b) L. L. Ingraham, *ibid.*, pp 497–509; (c) G. W. Buchanan, G. Montaudo, and P. Finocchiaro, *Can. J. Chem.*, **51**, 1053 (1973); (d) T. Holm and I. Crossland, *Acta Chem. Scand.*, **25**, 59 (1971); (e) D. Liebfritz, *Chem. Ber.*, **108**, 3014 (1975).

(11) R. C. Fuson, M. D. Armstrong, W. E. Wallace, and J. W. Kneisley [*J. Am. Chem. Soc.*, **66**, 681 (1944)] reported the formation of the olefin **15** from reaction of ketone **3** with MeMgI in boiling PhH.

(12) T. I. MacDonald and W. C. Still, *J. Am. Chem. Soc.*, **97**, 5280 (1975).

(13) R. L. Kieft, D. P. Novak, and T. L. Brown, *J. Organomet. Chem.*, **77**, 299 (1974).

(14) (a) For a recent review, see B. J. Wakefield, "The Chemistry of Organolithium Compounds", Pergamon Press, Elmsford, N.Y., 1974, pp 3–18. (b) L. D. McKeever, R. Waack, M. A. Doran, and E. B. Baker [*J. Am. Chem. Soc.*, **91**, 1057 (1969)] found that at −80 °C a THF solution of MeLi (enriched in ^{13}C) exhibited a multiplet ($J_{^{13}C-^{7}Li} = 15$ Hz) in its ^{7}Li NMR spectrum. In THF solution this multiplicity collapsed as the temperature was raised above −45 °C.

(15) The Cu(I) complex **20** was described by P. Hemmerich and C. Sigwart [*Experientia*, **19**, 488 (1963)] who reported this material to be very effective for the formation of Cu(I) complexes with oxygen-containing ligands.

(16) G. H. Posner and D. J. Brunelle, *J. Org. Chem.*, **38**, 2747 (1973).

(17) G. M. Whitesides, W. F. Fischer, Jr., J. San Filippo, Jr., R. W. Bashe, and H. O. House, *J. Am. Chem. Soc.*, **91**, 4871 (1969).

(18) All melting points are corrected and all boiling points are uncorrected. Unless otherwise stated $MgSO_4$ was employed as a drying agent. The ir spectra were determined with a Perkin-Elmer Model 257 infrared recording spectrophotometer fitted with a grating. The uv spectra were determined with a Cary Model 14 or a Perkin-Elmer Model 202 recording spectrophotometer. The ^{1}H NMR spectra were determined at 60 MHz with a Varian Model A-60 or Model T-60-A NMR spectrometer and the ^{13}C NMR spectra were determined at 100 MHz with a JEOL Fourier transform spectrometer, Model PFT-100. The chemical shift values are expressed in δ values (ppm) relative to a Me_4Si internal standard. The mass spectra were obtained with an Hitachi (Perkin-Elmer) Model RMU-7 or a Varian Model M-66 mass spectrometer. All reactions involving strong bases or reactive organometallic intermediates were performed under a nitrogen atmosphere.

(19) G. M. Whitesides, C. P. Casey, and J. K. Krieger, *J. Am. Chem. Soc.*, **93**, 1379 (1971).

(20) G. Wittig and A. Hesse, *Org. Synth.*, **50**, 66 (1970).

(21) (a) H. O. House, E. Feng, and N. P. Peet, *J. Org. Chem.*, **36**, 2371 (1971); (b) H. O. House, D. Koepsell, and W. Jaeger, *ibid.*, **38**, 1167 (1973).

(22) The composition of the crystalline solvates from LiX (X = Br or ClO_4) and DME as $LiX(DME)_2$ was established by dissolving known weights of $LiX(DME)_2$ and toluene in CD_3COCD_3 and then measuring the areas under the toluene (δ 2.30 and 7.15) and DME (δ 3.30 and 3.50) NMR peaks.

(23) H. O. House and J. E. Oliver, *J. Org. Chem.*, **33**, 929 (1968).

(24) H. O. House, R. A. Latham, and G. M. Whitesides, *J. Org. Chem.*, **32**, 2481 (1967).

(25) (a) R. C. Fuson and W. C. Hammann, *J. Am. Chem. Soc.*, **73**, 1851 (1951); (b) I. I. Lapkin, M. G. Shklyaeva, G. A. Koryakina, and O. N. Vinokurova, *J. Gen. Chem. USSR* (*Engl. Transl.*), **17**, 1337 (1947).

(26) H. O. House and E. F. Kinloch, *J. Org. Chem.*, **39**, 1173 (1974).

(27) G. Pfister and J. Bonastre [*Bull. Soc. Chim. Fr.*, 2053 (1966)] report $E_{1/2}$ values of −1.07 to −1.58 V for solutions of the ketone **3** in aqueous EtOH containing various buffers.

(28) H. O. House and W. F. Fischer, Jr., *J. Org. Chem.*, **33**, 949 (1968).

(29) L. S. Trzupek, T. L. Newirth, E. G. Kelly, N. E. Sbarbati, and G. M. Whitesides, *J. Am. Chem. Soc.*, **95**, 8118 (1973).

(30) The EPR spectra were obtained with a Magnion Model MVR-12X EPR spectrometer. We are indebted to Professor Ronald H. Felton for measuring these spectra.

(31) The EPR spectra of the ketyl **10** in various solvents with various counterions are described by P. B. Ayscough and R. Wilson, *J. Chem. Soc.*, 5412 (1963).

(32) The EPR spectrum of the K^+ analogue of ketyl **16** has been described by K. Maruyama, R. Tanikaga, and R. Goto, *Nippon Kagaku Zasshi*, **84**, 75 (1963).

(33) (a) O. Cervinka, V. Suchan, and B. Masar, *Collect. Czech. Chem. Commun.*, **30**, 1693 (1965); (b) R. F. Rekker and W. T. Nauta [*Recl. Trav. Chim. Pays-Bas*, **87**, 1099 (1968)] report for alcohol **17** λ_{max} 216 nm (log ϵ 4.20) and 265 (2.65).

(34) This result corresponds to our previous observation[9a] that cinnamonitrile is recovered unchanged after treatment with etheral Me_2CuLi at 0–10 °C for 20 min.

(35) The Raman spectra were determined with a Spex monochromator, Model 1401, employing a CR-3 argon ion laser as a light source. We are indebted te Professor Nai-Teng Yu and his associates for performing these measurements.

(36) The analogous infrared bands for DME solutions of $Ph_2C{=}O$ and $Ph_2\dot{C}{-}O^-Na^+$ (or K^+) are reported to be 1664 ($C{=}O$) and 1598 cm^{-1} (Ph) and 1554 ($C{=}O$) and 1581 cm^{-1} (Ph), respectively. The $C{=}O$ absorption for $Ph_2\dot{C}{-}O^-Li^+$ in DME was found to be 1563 cm^{-1} in concentrated solution and 1617 cm^{-1} in dilute solution. See (a) D. H. Eargle, Jr., and E. W. Cox, "The Alkali Metals", *Chem. Soc., Spec. Publ.*, **No. 22**, 116–124 (1967); (b) D. H. Eargle, Jr., *J. Chem. Soc. B*, 1556 (1970); (c) D. H. Eargle, Jr., and R. Emrich, *J. Org. Chem.*, **35**, 3744 (1970).