blocking groups to restrain ground-state reactivity. Should methods be found to circumvent this, a number of useful procedures would become available.

Use of Lithium Organocuprate Additions as Models for an Electron-Transfer Process

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The addition of nucleophiles, $N:^-$, to unsaturated carbonyl compounds, 1 (or other electrophiles), can occur either by direct nucleophilic addition to form the product 4 or as a two-stage reaction in which only an electron is transferred from $N:^-$ to 1 in the first stage. Subsequent coupling of radical intermediates 2 and 3 to form 4 constitutes the second stage of this latter process. A distinction between these mechanistic possibilities has several practical consequences.

In the two-stage pathway, the equilibrium position for the first step, the reversible transfer of an electron, can be estimated from the electrode potential, E_{ox}, for oxidation (loss of an electron) of the nucleophile, $N:^-$, and the corresponding potential, E_{red}, for reduction (gain of an electron) of the carbonyl compound 1. The electrode potentials, E_{ox} and E_{red}, used in this Account refer to the potential, measured by standard polarographic or cyclic voltammetry techniques in an aprotic solvent (usually dimethylformamide) with respect to a saturated calomel electrode, associated with the following reaction: oxidized reactant + $e^- \rightleftarrows$ reduced reactant. With this sign convention, the most powerful reducing agents, $N:^-$, have the most negative E_{ox} values and the most difficultly reduced unsaturated carbonyl compounds 1 have the most negative E_{red} values. Thus, when the value $E_{red} - E_{ox}$ is positive, transfer of an electron from $N:^-$ to the carbonyl compound 1 is energetically favorable.

To obtain sufficient concentrations of intermediates 2 and 3 (ca. 10^{-3} M or greater) so that the second coupling reaction, $2 + 3 \rightarrow 4$, can occur at a reasonable rate, the electrode potential difference, $E_{red} - E_{ox}$, should be more positive than -0.4 V. Consequently, any reaction that proceeds only by the two-stage process would be expected to fail (or to proceed very slowly) if structural changes in $N:^-$ and/or the enone 1 cause the potential difference $E_{red} - E_{ox}$ to become more negative than -0.4 V.

For reactions that can occur by either pathway, the mechanism would be expected to change with structural changes in the reactants that cause the value, $E_{red} - E_{ox}$, to change from values more negative than ca. -0.4 V to more positive values. Of particular importance is the possibility that this change in mechanism may be accompanied by a change in product structure since the charge densities in the original reactants 1 and $N:^-$ and the spin densities in the radical intermediates 2 and 3 may differ. Thus, the locations of highest spin density in the intermediates 2 and 3 could be useful in predicting the structure of the major product formed by a two-stage reaction.
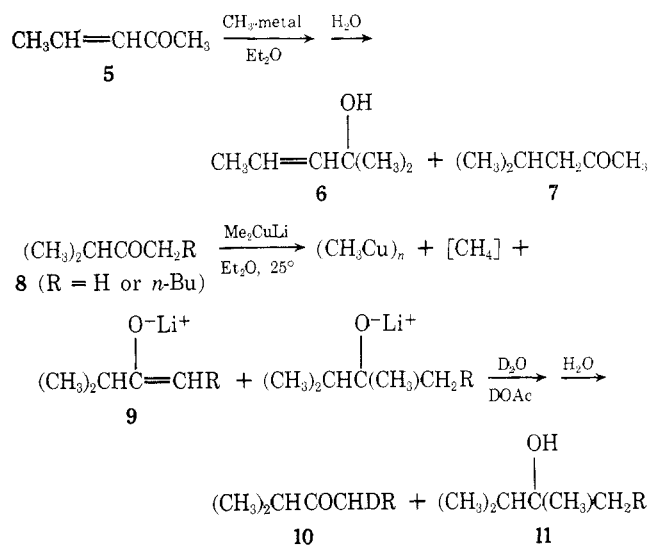
Finally, in any two-stage reaction where the rate of electron transfer is comparable to or more rapid than the subsequent coupling of intermediates 2 and 3, the lifetime of these intermediates may be sufficient to allow other reactions to intervene. For example, one or both of these intermediates 2 or 3 might dimerize or might undergo a stereochemical or structural rearrangement prior to coupling.

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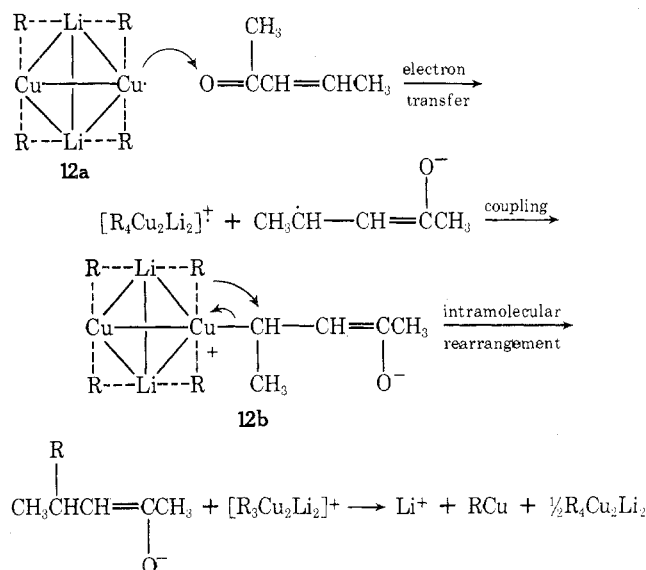
Conjugate Addition Reactions of Lithium Organocuprates

The relative rates of reaction of the enone **5** with MeLi (to form **6**) and with MeCuP(Bu-n)$_3$ (to form **7**) were both substantially faster than the addition of MeMgBr (to form **6** and **7**).[1] However, saturated ketones, which also reacted rapidly with Grignard reagents, failed to react with MeCuP(Bu-n)$_3$ and reacted only slowly with the more reactive reagent, Me$_2$CuLi.[1] For example, the ketones **8** reacted with Me$_2$CuLi to form a mixture of an enolate and an alkoxide; quenching with D$_2$O–DOAc gave the deuterio ketones **10** accompanied by the alcohols **11**.[2] Thus, the organocopper(I) reagents exhibited the curious behavior of apparently being very reactive nucleophiles in additions to unsaturated carbonyl compounds but poor nucleophiles in additions to nonconjugated carbonyl compounds.

$$CH_3CH=CHCOCH_3 \xrightarrow[Et_2O]{CH_3\text{-metal}} \xrightarrow{H_2O}$$

5

$$\underset{OH}{CH_3CH=CH\overset{|}{C}(CH_3)_2} + (CH_3)_2CHCH_2COCH_3$$

6 **7**

$$(CH_3)_2CHCOCH_2R \xrightarrow[Et_2O,\ 25°]{Me_2CuLi} (CH_3Cu)_n + [CH_4] +$$

8 (R = H or n-Bu)

$$(CH_3)_2CH\overset{O^-Li^+}{\overset{|}{C}}=CHR + (CH_3)_2CH\overset{O^-Li^+}{\overset{|}{C}}(CH_3)CH_2R \xrightarrow[DOAc]{D_2O} \xrightarrow{H_2O}$$

9

$$(CH_3)_2CHCOCHDR + (CH_3)_2CH\overset{OH}{\overset{|}{C}}(CH_3)CH_2R$$

10 **11**

Both this seemingly contradictory behavior and various other observations[1a,3] have led us to believe that the conjugate addition of lithium organocuprates to unsaturated carbonyl compounds[4] is an example of a two-stage reaction involving an initial electron transfer. The R groups of various R$_2$CuLi reagents are transferred with retention of configuration,[5] excluding the intermediacy of an R· free radical and supporting the presence of an intermediate such as **12b** in which the group R is transferred from the cuprate to the carbonyl compound by an intramolec-

(1) (a) H. O. House, W. L. Respess, and G. M. Whitesides, *J. Org. Chem.*, **31**, 3128 (1966); (b) H. O. House and D. D. Traficante, *ibid.*, **28**, 355 (1963); H. O. House, D. D. Traficante, and R. A. Evans, *ibid.*, **28**, 348 (1963).

(2) H. O. House, C. Y. Chu, J. M. Wilkins, and M. J. Umen, *J. Org. Chem.*, **40**, 1460 (1975).

(3) (a) H. O. House and M. J. Umen, *J. Am. Chem. Soc.*, **94**, 5475 (1972); *J. Org. Chem.*, **38**, 3893 (1973). (b) The suggestion has been made (ref 5a) that the E_{red} values of unsaturated carbonyl compounds might correlate with the ability of these substrates to add nucleophiles in a conjugate manner (e.g., the Michael reaction). However, perusal of the various E_{red} values that have been obtained (ref 2, 3, 9, 11) has not revealed any obvious correlations; the most reactive Michael acceptors appear to be those α,β-unsaturated carbonyl compounds that lack β substituents or other substituents that would interfere sterically with the conjugate addition of a nucleophile.

(4) (a) For a comprehensive review, see G. H. Posner, *Org. React.*, **19**, 1 (1972); (b) G. H. Posner and D. J. Brunelle, *J. Org. Chem.*, **38**, 2746 (1973).

(5) (a) G. M. Whitesides and P. W. Kendall, *J. Org. Chem.*, **37**, 3718 (1972); also see C. R. Johnson and G. A. Dutra, *J. Am. Chem. Soc.*, **95**, 7783 (1973); (b) F. Näf and P. Degen, *Helv. Chim. Acta*, **54**, 1939 (1971); F. Näf, P. Degen, and G. Ohloff, *ibid.*, **55**, 82 (1972); (c) C. P. Casey and R. A. Boggs, *Tetrahedron Lett.*, 2455 (1971).
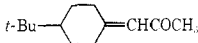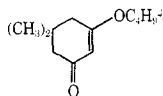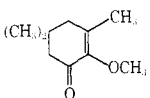
Scheme I

ular rearrangement.

The limited structural information presently available[1a,6] suggests that the cuprate reagents should be formulated as dimers, R$_4$Cu$_2$Li$_2$, with all R groups equivalent. This information, taken with the facts that both RCu compounds[7] and many RLi compounds[8] have tetrameric metal clusters (either planar or tetrahedral) with bridging alkyl groups, led us to adopt structure **12a** as a working hypothesis for lithium organocuprates. Using this structural hypothesis, we suggest the reaction pathway indicated in Scheme I to account for the various facts concerning the reaction of lithium organocuprates with unsaturated carbonyl compounds.

Alternatively, conjugate addition has been suggested[5a] to proceed by direct nucleophilic addition of the cuprate **12a** to form the intermediate **12b**, a process analogous to that believed operative in most reactions of cuprate reagents with alkyl halides[9a] and alkyl tosylates.[5a] We believe that this alternative mechanism does not adequately account either for the very large kinetic preference for conjugate addition rather than 1,2 addition of cuprate reagents or for a number of other subsequently described experimental observations.

The two-stage mechanism (Scheme I) requires a relationship between the success or failure of the reaction and the value of the potential difference, $E_{red} - E_{ox}$. With a given cuprate reagent (e.g., Me$_2$CuLi), when the reduction potential of the carbonyl compound (e.g., E_{red} for **1** → **2**) becomes sufficiently negative, conjugate addition should no longer occur. This
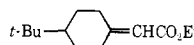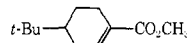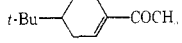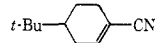
(6) G. van Koten and J. G. Noltes, *J. Chem. Soc., Chem. Commun.*, 940 (1972).

(7) (a) G. von Koten, A. J. Leusink, and J. G. Noltes, *Chem. Commun.*, 1107 (1970); J. M. Guss, R. Mason, I. Sotofte, G. van Koten, and J. G. Noltes, *J. Chem. Soc., Chem. Commun.*, 446 (1972); G. van Koten and J. G. Noltes, *J. Organometal. Chem.*, **84**, 129 (1973); (b) J. A. J. Jarvis, B. T. Kilbourn, R. Pearce, and M. F. Lappert, *J. Chem. Soc., Chem. Commun.*, 475 (1973).

(8) (a) E. B. Baker, L. D. McKeever, R. Waack, and M. A. Doran, *J. Am. Chem. Soc.*, **90**, 3244 (1968); (b) T. L. Brown, L. M. Seitz, and B. Y. Kimura, *ibid.*, **90**, 3245 (1968); T. L. Brown, *Acc. Chem. Res.*, **1**, 23 (1968).
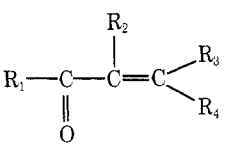
(9) (a) G. M. Whitesides, W. F. Fischer, Jr., J. San Filippo, Jr., R. W. Bashe, and H. O. House, *J. Am. Chem. Soc.*, **91**, 4871 (1969); (b) G. M. Whitesides, J. San Filippo, Jr., C. P. Casey, and E. J. Panek, *ibid.*, **89**, 5302 (1967); (c) D. E. Bergbreiter and G. M. Whitesides, *ibid.*, **96**, 4937 (1974); (d) W. H. Mandeville and G. M. Whitesides, *J. Org. Chem.*, **39**, 400 (1974).
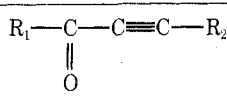
Table I
Results of Treating Various Unsaturated Carbonyl Compounds with $(CH_3)_2CuLi$ in Ether[a]

Forms conjugate adduct		Forms conjugate adduct	
$PhCH=CHCOCH_3$	(−1.64)	$CH_3CH=CHCO_2CH_3$	(−2.33)
$(CH_3)_2C=C(CO_2Et)_2$	(−2.13)	$(CH_3)_2C=C(CH_3)COCH_3$	(−2.35)
$CH_3CO_2C(CH_3)=C(CH_3)COCH_3$	(−2.14)	**Recovered**	

Base value column and increment tables below.

		Forms conjugate adduct (continued)	
t-Bu—⬡=CHCOCH₃	(−2.12)	(CH₃)₂ ⬡ OC₃H₇-i (O)	(−2.43)
(CH₃)₂ ⬡ CH₃ OCH₃ (O)	(−2.20)	t-Bu—⬡=CHCO₂Et	(−2.54)
n-$PrC\equiv CCO_2CH_3$	(−2.26)	t-Bu—⬡—CO₂CH₃	(−2.50)
t-Bu—⬡—COCH₃	(−2.25)	t-Bu—⬡—CN	(−2.55)

[a] E_{red} values in volts vs. SCE measured in an aprotic solvent.

Scheme II
Estimation of E_{red} for
α,β-Unsaturated Carbonyl Compounds[a]

Base value −1.9 V

Substituent	R_1	R_2	R_3 or R_4
Alkyl	−0.1	−0.1	−0.1
First alkoxyl	−0.3	0	−0.3
First phenyl	+0.4	+0.1	+0.4

R_1—C—C≡C—R_2 (‖ O) Base value −1.8 V

Substituent	R_1	R_2
Alkyl	−0.1	−0.1
First alkoxyl	−0.3	Not determined

Suggested base value −2.3 V for $R_2C=C(R)—C\equiv N$

[a] E_{red} values in volts vs. SCE in an aprotic solvent.

result was observed when a series of unsaturated carbonyl compounds were treated with ethereal Me_2Cu-Li (Table I). Compounds with E_{red} values less negative than −2.4 V underwent conjugate addition, whereas compounds with E_{red} values more negative than −2.4 V were recovered unchanged.[3] While this potential–reactivity correlation is clearly compatible with a process requiring initial reduction of an unsaturated carbonyl compound 1 to its anion radical 2, we have been unable to discern any obvious relationship between the E_{red} values for various unsaturated carbonyl compounds and their reactivity as acceptors in Michael reactions (nucleophilic additions of carbanionic intermediates).[3b]

The synthetic utility of such correlations lies in the ability to predict whether a given lithium organocuprate is likely to add to an unsaturated carbonyl compound from a knowledge of the reduction potential, E_{red}, of the carbonyl reactant. To facilitate use of this correlation in planning a possible synthetic sequence, the simple empirical rules summarized in

Scheme II provide estimates of E_{red} values for unsaturated carbonyl compounds that are usually reliable to within ±0.1 V.[10]

A knowledge of the potentials, E_{ox}, associated with the oxidation of cuprate reagents 13 containing various R substituents is clearly desirable. Estimates of the E_{ox} values associated with the oxidation steps 13 → 14 and 14 → 15 can be derived from several reactions of cuprates. The successful conjugate addition of $Me_2Cu_2Li_2$ only to substrates having E_{red} values less negative than −2.4 V, considered with the idea that the value $E_{red} - E_{ox}$ should be less negative than −0.4 V, suggests that the value of E_{ox} of the first step, 13 → 14, in the oxidation of $Me_4Cu_2Li_2$ is about −1.9 V. When lithium organocuprates, 13, are treated with various oxidants [e.g., O_2, $PhNO_2$, or Cu(II) salts] having electrode potentials, E_{ox} more positive than −1.2 V, a two-electron oxidation occurs (presumably via intermediates 14 and 15) to form coupled products, 16,[3,9] suggesting an E_{ox} value of ca. −1.0 V for the second oxidation step, 14 → 15. It is apparently this possibility for transferring two electrons that leads to reduction products rather than conjugate addition products when very easily reduced unsaturated carbonyl compounds [e.g., $(EtO_2C)_2C=C(CO_2Et)_2$, E_{red} −0.97 V (first electron) and −1.10 V (second electron)] are treated with Me_4-Cu_2Li_2.[3a] Although studies with other cuprates are presently incomplete, the most negative enone E_{red} values that permit successful reaction appear to be: $(allyl)_2CuLi$, −2.1 V;[11a] Ph_2CuLi, −2.3 V;[11b] Me_2Cu-Li, −2.35 V;[2,3] and $(vinyl)_2CuLi$, ca. −2.4 V.[2]

$$R_4Cu_2Li_2 \xrightarrow{-e^-} [R_4Cu_2Li_2]^+ \xrightarrow{-e^-} [R_4Cu_2Li_2]^{2+} \longrightarrow$$
$$\quad\; 13 \qquad\qquad\; 14 \qquad\qquad\quad 15$$
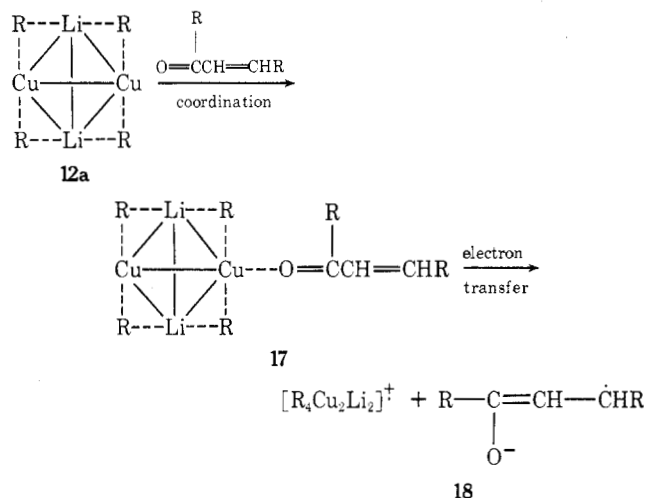
$$R—R + 2Li^+ + 2RCu$$
$$16$$
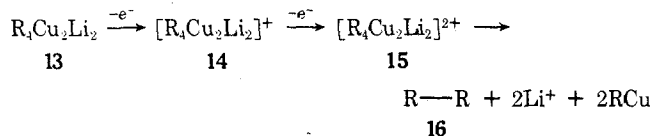
Our efforts to obtain the value of E_{ox} for Me_4-Cu_2Li_2 by electrochemical measurement were frustrated by the failure to observe any oxidative current

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

(11) (a) H. O. House and W. F. Fischer, Jr., *J. Org. Chem.*, **34**, 3615, 3626 (1969); (b) H. O. House and J. M. Wilkins, to be published; (c) H. O. House and P. D. Weeks, *J. Am. Chem. Soc.*, **97**, 2770, 2778, 2785 (1975); (d) H. O. House and C. Y. Chu, to be published.

Scheme III

R---Li---R R
 \ / | \ | |
Cu——Cu   O=CCH=CHR
 / \ | / | coordination
R---Li---R

12a

R---Li---R R
 \ / | \ | |
Cu——Cu---O=CCH=CHR →electron transfer→
 / \ | / |
R---Li---R

17

$[R_4Cu_2Li_2]^+$ + R—C=CH—ĊHR
                                |
                                O⁻

18

Table II
Electrode Potentials for the Oxidation of Various Common Carbanionic Nucleophiles and Reducing Agents

Compound	Solvent	E_{ox}, V, vs. SCE
Na	HMP	−2.96
$Cr(en)_2(OAc)_2$	DMF	−1.59
$Ph_3C^-Li^+$	DME	−1.3 (−1.4)[a]
$Ph_2CH^-Li^+$	DME	−1.1
$PhCH=CCH, Na^+$ (O⁻)	DMF	−0.2
CH^-Li^+ (cyclopentadienyl)	DME	−(−0.1)[a]
$(EtO_2C)_2CH^-Na^+$	DMF	+0.4

[a] Calculated from data in ref 12c.

during attempted electrolysis of $Me_4Cu_2Li_2$ solutions throughout the range −0.5 to −2.5 V.[11d] However, these same solutions are capable of transferring an electron to *reactants containing a carbonyl group* that are reduced within this potential range. For example, both fluorenone[1a] (E_{red} = −1.29 and −1.95 V) and benzophenone[11d] (E_{red} = −1.80 and −2.34 V) react with ethereal solutions of $Me_4Cu_2Li_2$ to give relatively stable solutions of the corresponding radical anions that react only slowly to form adducts. Consequently, we believe that the transfer of an electron from the cuprate reagent to a metal electrode (required for successful electrochemical measurement) is kinetically very slow and that rapid electron transfer from cuprate reagents requires prior coordination of the carbonyl component with the cuprate metal cluster such as structure **17** in Scheme III. If dissociation of this complex **17** with electron transfer (a process analogous to inner-sphere electron transfer in redox reactions of metal ions) to form anion radical **18** is energetically favorable, this transfer presumably occurs followed by the steps indicated in Scheme I. In reactions with saturated ketones (e.g., **8**) where dissociation of a complex analogous to **17** would be energetically unfavorable (E_{red} more negative than −2.9 V for saturated ketones), the complex **17** may serve as the intermediate leading to the formation of enolate anions **9** or to a slow 1,2 addition producing alcohols **11**.

The need for initial coordination of $Me_4Cu_2Li_2$ with a doubly bound oxygen (e.g., **17**) is indicated by the observation that substrates without this functionality such as cinnamonitrile (E_{red} = −1.84 V)[3a] or anthracene (E_{red} = −1.93 V)[11d] fail to react with $Me_4Cu_2Li_2$. However, substrates reduced with comparable difficulty that have a doubly bound oxygen function (e.g., Table I and PhCH=CHSO$_2$C$_6$H$_4$Cl-*p*,[4b] E_{red} = −1.70 V) do yield conjugate addition products with $Me_4Cu_2Li_2$.

Use of E_{ox} Values and Spin Density Measurements

A survey of the E_{ox} values for several common carbanionic nucleophiles and reducing agents is collected (Table II).[11c,12] The values obtained are consistent with the expectation that the most negative electrode potentials are found with carbanions such as Ph_3C:⁻ that can be oxidized to rather stable free radicals (e.g., $Ph_3C\cdot$). Simple enolate anions have E_{ox} values (−0.2 to +0.4 V) sufficiently positive that reaction with typical unsaturated carbonyl compounds (E_{red} = −1.4 to −2.5 V) by an electron-transfer process is most improbable. Although our efforts to measure directly E_{ox} values for several common main-group metal derivatives (e.g., MeLi, Me$_2$Mg, LiAlH$_4$) have not been successful,[13] two subsequently discussed reactions of these reagents with simple enones suggest that these reactions also do not occur by initial electron transfer. Inspection of E_{ox} values for organometallic compounds[14] suggests that various transition-metal derivatives tend to be most easily oxidized (typical E_{red} values −1.0 to −2.5 V) and are, therefore, the classes of compounds most likely to react with electrophiles by an electron-transfer process. This facile oxidation of transition-metal derivatives presumably reflects the availability of two or more relatively stable valence states.

Since the E_{ox} value for $Ph_3C^-Li^+$ is sufficiently negative (−1.3 V) to permit electron transfer with easily reduced enones, we examined the reaction[11c] of this reagent with a readily reduced enone, **19**, and with a difficultly reduced enone, **20**. EPR studies[15] of the radical $Ph_3C\cdot$ suggest that about 65% of the spin density is located at the central carbon atom. In the corresponding carbanion from Ph_3CLi, only 13% (^{1}H NMR spectrum)[16] to 38% (^{13}C NMR spectrum)[17] of the negative charge appears to be located at the central carbon atom. The values suggest that the trityl radical may have more tendency to couple with another radical at the central carbon than would be the case for reaction of the trityl anion with an electro-

(12) (a) 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); (b) H. O. House, R. W. Giese, K. Kronberger, J. P. Kaplan, and J. F. Simeone, *ibid.*, **92**, 2800 (1970); (b) R. Breslow and S. Mazur, *ibid.*, **95**, 584 (1973); (d) H. O. House and E. F. Kinloch, *J. Org. Chem.*, **39**, 1173 (1974).

(13) From a study of the electrochemical oxidation of several R$_2$Mg compounds by T. Psareas and R. E. Dessy [*J. Am. Chem. Soc.*, **88**, 5132 (1966)], we estimate the electrode potentials vs. SCE to be about −0.7 V.
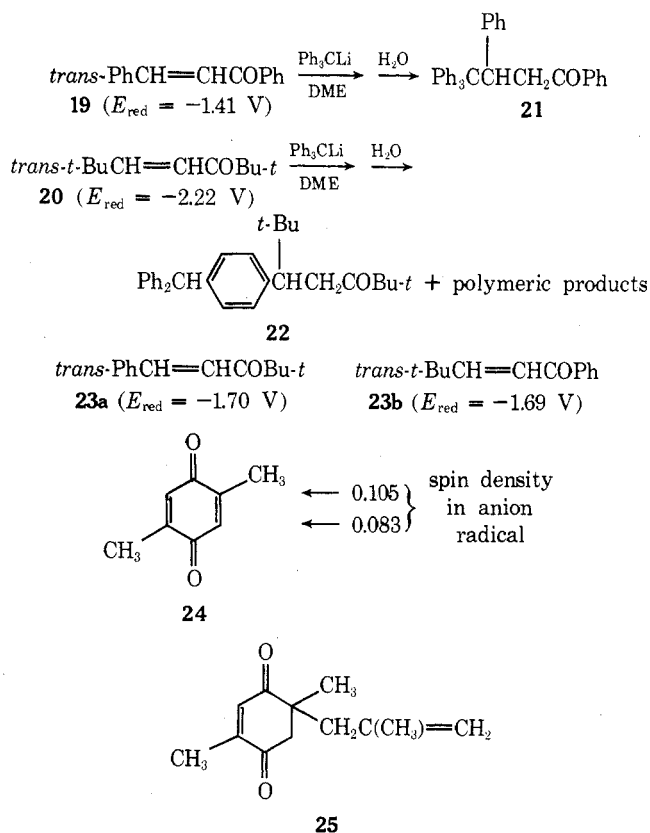
(14) C. K. Mann and K. K. Barnes, "Electrochemical Reactions in Nonaqueous Systems," Marcel Dekker, New York, N.Y., 1970, pp 403–446.

(15) (a) D. B. Chesnut and G. J. Sloan, *J. Chem. Phys.*, **33**, 637 (1960); **35**, 443 (1961); (b) P. B. Ayscough, A. P. McCann, and R. Wilson, *Proc. Chem. Soc., London*, 16 (1961).

(16) (a) V. R. Sandel and H. H. Freedman, *J. Am. Chem. Soc.*, **85**, 2328 (1963); (b) J. B. Grutzner, J. M. Lawlor, and L. M. Jackman, *ibid.*, **94**, 2306 (1972).

(17) H. O. House, A. V. Prabhu, and W. V. Phillips, to be published.

phile.[18] Reaction of Ph₃CLi with the enone **19** (E_{red} − E_{ox} = −0.1 V, electron transfer favorable) occurred in less than 10 min to form the adduct **21** (80% yield). However, the red color of the Ph₃C⁻ anion was not discharged even after reaction with the enone **20** (E_{red} − E_{ox} = −0.9 V, electron transfer unlikely) for 4 hr. In this latter case the products were the monomeric adduct **22** (23% yield) and a mixture of polymeric materials.

trans-PhCH=CHCOPh $\xrightarrow[\text{DME}]{\text{Ph}_3\text{CLi}}$ $\xrightarrow{\text{H}_2\text{O}}$ Ph₃CCHCH₂COPh

19 (E_{red} = −1.41 V)　　　　　　　　　**21**

trans-t-BuCH=CHCOBu-t $\xrightarrow[\text{DME}]{\text{Ph}_3\text{CLi}}$ $\xrightarrow{\text{H}_2\text{O}}$

20 (E_{red} = −2.22 V)

Ph₂CH⟨⟩CHCH₂COBu-t + polymeric products

22

trans-PhCH=CHCOBu-t　　　trans-t-BuCH=CHCOPh

23a (E_{red} = −1.70 V)　　**23b** (E_{red} = −1.69 V)

24

← 0.105 ⎫ spin density
← 0.083 ⎭ in anion radical

25

Although these results appeared encouraging, comparable studies of the reaction of Ph₃CLi with the isomeric enones **23** (E_{red} − E_{ox} = −0.4 V, electron transfer favorable in each case) revealed that although both enones **23** reacted rapidly with Ph₃CLi, the product from **23a** had a structure analogous to **21** whereas the product from **23b** had a structure analogous to **22**. Consequently, although the relative reaction rates are compatible with the idea that enones **19** and **23**, but not **20**, are capable of reaction by an electron-transfer process, the structures of the products (**21** or **22**) are apparently determined by the amount of steric hindrance at the β carbon and not by electron density differences in the trityl anion and the trityl radical.
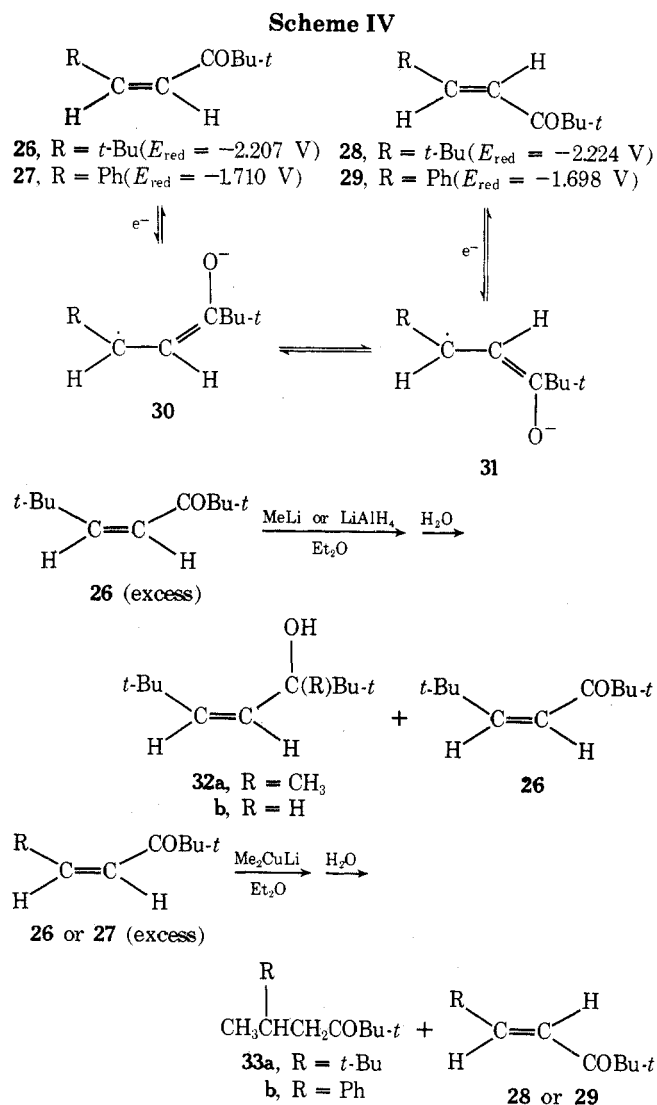
Another example suggesting a possible correlation of product structure with the spin density of radical intermediates from electron transfer is provided by a study of the reaction of easily reduced quinones (E_{red} values less negative than −0.7 V) with π-methallylnickel bromide.[19] Quinones such as **24** (spin density of anion radical indicated) reacted to form products

such as **25** in which coupling with the methallyl group had occurred at the site of higher spin density.

Stereochemical Isomerization of Radical Anion Intermediates

Although a knowledge of appropriate E_{red} and E_{ox} values can be used to decide whether a reaction proceeding by initial electron transfer is energetically reasonable, it is uncertain whether a correlation of product structures with the spin density of radical intermediates provides evidence for an electron-transfer process. Consequently, other experimental tests were needed to distinguish between the two mechanisms under consideration. The less stable cis enones **26** and **27** (Scheme IV),[12a,b] when converted to the corresponding anion radicals **30**, very rapidly equilibrated via the trans anion radicals **31** to the trans enones **28** and **29**. Because electron exchange between anion radicals and the corresponding precursors is very rapid (typically $10^9 M^{-1} \text{sec}^{-1}$),[20] the presence of even a small concentration of one of the anion radicals **30** or **31** can catalyze the practically complete isomerization of the cis enones **26** or **27** to the trans isomers **28** or **29**.

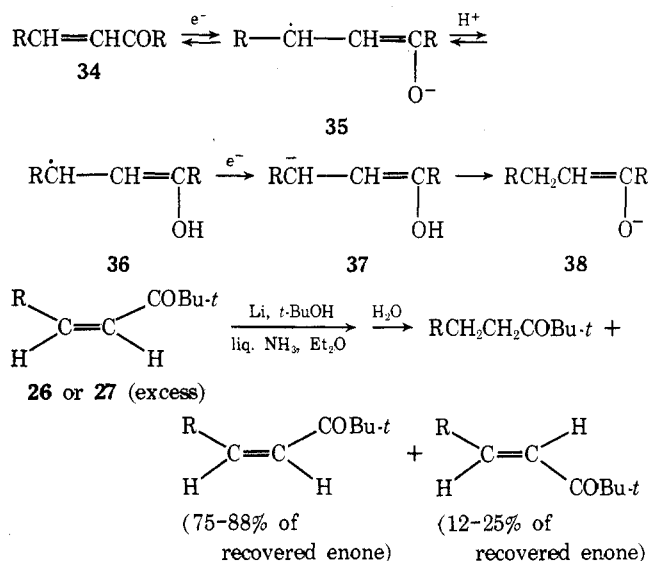The results to be expected in reactions proceeding

Scheme IV

26, R = t-Bu(E_{red} = −2.207 V)　**28**, R = t-Bu(E_{red} = −2.224 V)
27, R = Ph(E_{red} = −1.710 V)　**29**, R = Ph(E_{red} = −1.698 V)

30　　　　　　　　　　　**31**

t-Bu—C=C—COBu-t / H, H　**26** (excess)　$\xrightarrow[\text{Et}_2\text{O}]{\text{MeLi or LiAlH}_4}$ $\xrightarrow{\text{H}_2\text{O}}$

32a, R = CH₃
b, R = H　　　　　　　　**26**

R—C=C—COBu-t / H, H　**26 or 27** (excess)　$\xrightarrow[\text{Et}_2\text{O}]{\text{Me}_2\text{CuLi}}$ $\xrightarrow{\text{H}_2\text{O}}$

CH₃CHCH₂COBu-t +
│
R

33a, R = t-Bu
b, R = Ph　　　　　　　　**28 or 29**

(18) Examples of the reaction of trityllithium with carbonyl compounds at both the central carbon and at a para position are known: P. Tomboulian and K. Stehower, *J. Org. Chem.*, **33**, 1059 (1968).

(19) L. S. Hegedus and E. L. Waterman, *J. Am. Chem. Soc.*, **96**, 6789 (1974).

(20) For example, see N. Haran, Z. Luz, and M. Shporer, *J. Am. Chem. Soc.*, **96**, 4788 (1974).

Scheme V

$$RCH{=}CHCOR \underset{}{\overset{e^-}{\rightleftharpoons}} R{-}\overset{\cdot}{C}H{-}CH{=}\overset{|}{C}R \overset{H^+}{\rightleftharpoons}$$
34 **35**

$$\overset{\cdot}{R}CH{-}CH{=}\overset{|}{C}R \overset{e^-}{\longrightarrow} \overset{-}{R}CH{-}CH{=}\overset{|}{C}R \longrightarrow RCH_2CH{=}\overset{|}{C}R$$
OH / OH / O⁻
36 **37** **38**

$$\underset{H}{\overset{R}{>}}C{=}C\underset{H}{\overset{COBu\text{-}t}{<}} \xrightarrow[\text{liq. NH}_3,\ \text{Et}_2\text{O}]{\text{Li, }t\text{-BuOH}} \xrightarrow{\text{H}_2\text{O}} RCH_2CH_2COBu\text{-}t\ +$$
26 or **27** (excess)

$$\underset{H}{\overset{R}{>}}C{=}C\underset{H}{\overset{COBu\text{-}t}{<}} + \underset{H}{\overset{R}{>}}C{=}C\underset{COBu\text{-}t}{\overset{H}{<}}$$
(75–88% of recovered enone) (12–25% of recovered enone)

without initial electron transfer are illustrated by the reaction of a twofold excess of the cis enone **26** with LiAlH₄ or MeLi.[11c] In each case practically no stereochemical isomerization of the C–C double bond was observed either in the product **32** or in the recovered excess enone **26**. The corresponding reactions with the trans enone **28** produced alcohol products in which the trans stereochemistry of the C–C double bond was retained. Similar results were obtained from reaction of the more easily reduced cis enone **27** with MeLi.

In contrast, reaction of an excess of either cis enone **26** or **27** with Me₂CuLi produced the conjugate adduct **33** accompanied by trans enone **28** or **29** where stereochemical isomerization was practically complete.[11c] A comparable result was obtained from the conjugate reduction of excess cis enone **26** with the chromium(II) reagent, Cr(en)₂(OAc)₂.[11c,12d] Thus, in the cuprate and Cr(II) reactions, but not in the MeLi and LiAlH₄ reactions, there was clearly a species present in the reaction solution that rapidly isomerized the cis enones **26** and **27** to the trans isomers **28** and **29**.

A crude estimate of the minimum time required for the cis → trans enone isomerizations (**26** or **27** → **30** → **31** → **28** or **29**) was obtainable from studying the conjugate reduction of an excess of the cis enone **26** or **27** (Scheme V) with Li and *t*-BuOH in liquid NH₃, where the recovered excess enones were only partially isomerized from cis (**26** or **27**) to trans (**28** or **29**).[11c] Since the second electron-transfer step (**36** → **37**) in this reaction is believed[12a,b] to be responsible for the rapid consumption of the anion-radical intermediate **35**, the rates of enone isomerization and reduction of the radical **36** are apparently similar. A study[21] of the metal–ammonia reduction of a cis alkenyl chloride indicated that the rate of electron transfer from a metal–ammonia solution to a radical intermediate was comparable to the rate of equilibration of an α-substituted vinyl radical (less than 10⁸ sec⁻¹),[22] suggesting that the enone isomerization

(e.g., **26** → **30** → **31** → **28**) requires a time longer than 10⁻⁸ sec.

The foregoing data indicate that the cis → trans isomerization of certain unsaturated compounds can be used to detect the presence of radical-anion species in a reaction mixture[23] provided appropriate control experiments have demonstrated that ionic species in the reaction mixture do not cause stereochemical isomerization. However, this stereochemical test, like the detection of ion-radical species by EPR spectrometry, does not establish that radical species detected lie on the reaction path leading from reactants to products. Thus, one could imagine that although an enone, **1**, and a nucleophile, N:⁻, exist in equilibrium with small amounts of radical species **2** and **3**, the reaction leading to products **4** involves the direct nucleophilic addition of N:⁻ to the enone **1**.

Structural Isomerization of Radical-Anion Intermediates

An alternative chemical test might be devised if one examined reactions with an enone, **39**, in which the group R was capable of undergoing intramolecular structural rearrangement when the radical anion **40** was formed. If intramolecular rearrangement of the anion radical **40** is more rapid than coupling with N· to form the normal product **41**, then the reaction could be diverted from its normal course to form a rearranged product.

$$\underset{N}{\overset{|}{}}$$
$$RCH{-}CH{=}CBu\text{-}t$$
O⁻
41

$$RCH{=}CHCOBu\text{-}t \xrightarrow[\text{from N:}^-]{e^- \text{ transfer}} \overset{\cdot}{R}CH{-}CH{=}CBu\text{-}t$$
39 O⁻
40

intramolecular rearrangement

rearranged ← N· ← rearranged
product   radical anion
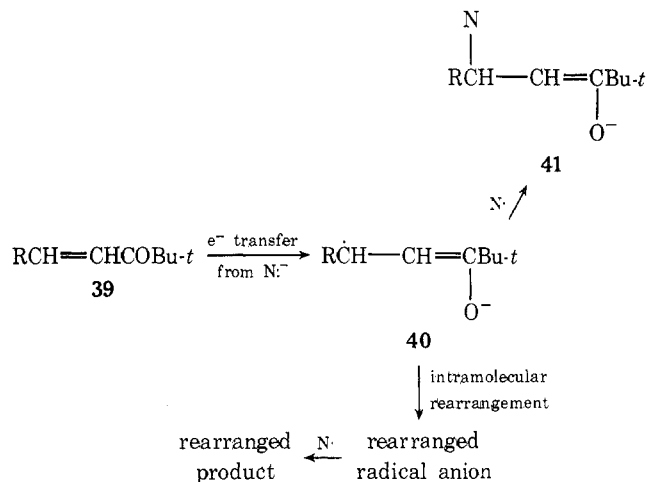
To explore this idea the two radical rearrangements[24] selected for study were the cyclization of a hexenyl radical, **42** → **43**, and the ring opening of a cyclopropylcarbinyl radical, **44** → **45** (Scheme VI). To study the possible rearrangement of radical anions such as **50** and **51** to **52** and **53**, the electrochemical reductions of enones **46**–**49**[11c,25] were studied. The E_{red} values of these enones (−2.16 to −2.20 V) do not differ significantly from the value (−2.22 V) for the enone **28** that forms a relatively stable anion radical **31** (half-life ca. 20 min).[12a] Cyclic voltammetry revealed that the radical anions derived from each of the enones **46**–**49** were also surprisingly stable, the
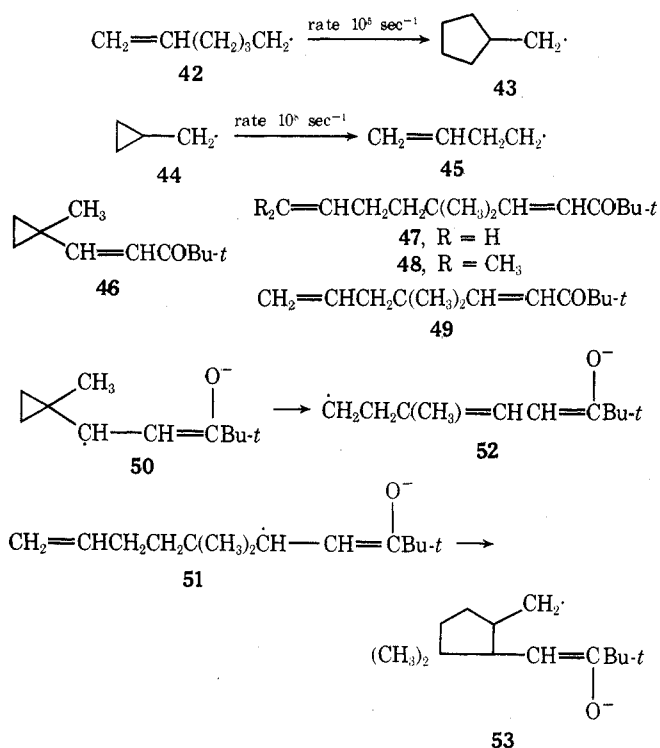
(21) (a) H. O. House and E. F. Kinloch, *J. Org. Chem.*, **39**, 747 (1974); also see (b) G. D. Sargent and M. W. Browne, *J. Am. Chem. Soc.*, **89**, 2788 (1967); (c) A. J. Fry and M. A. Mitnick, *ibid.*, **91**, 6207 (1969).

(22) L. A. Singer, *Sel. Org. Transform.*, **2**, 239 (1972).

(23) Other examples of the use of this general procedure include: (a) G. Levin, T. A. Ward, and M. Szwarc, *J. Am. Chem. Soc.*, **96**, 270 (1974); (b) Y. Ito, T. Konoike, and T. Saegusa, *Tetrahedron Lett.*, 1287 (1974).

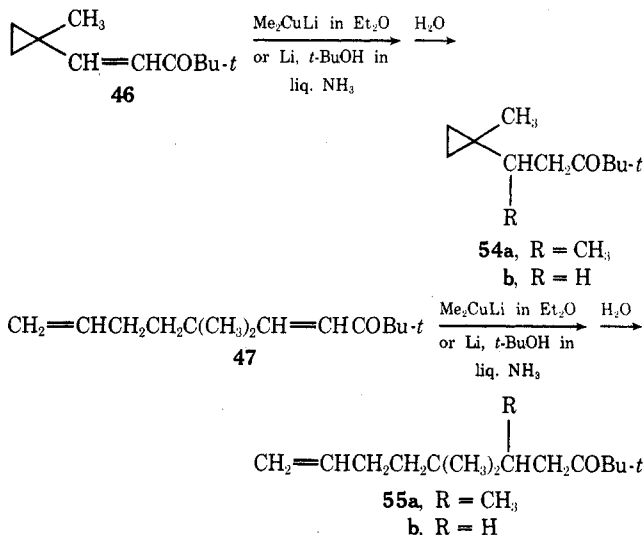(24) K. U. Ingold, *Free Radicals*, **1**, 37 (1973).

(25) H. O. House, W. C. Liang, and P. D. Weeks, *J. Org. Chem.*, **39**, 3102 (1974).
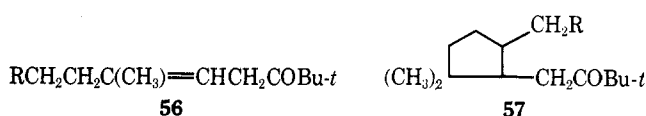
Scheme VI

$$CH_2\!\!=\!\!CH(CH_2)_3CH_2\cdot \xrightarrow{\text{rate }10^5\text{ sec}^{-1}} \text{(cyclopentyl)}\!\!-\!\!CH_2\cdot$$

42   **43**

$$\text{(cyclopropyl)}\!\!-\!\!CH_2\cdot \xrightarrow{\text{rate }10^8\text{ sec}^{-1}} CH_2\!\!=\!\!CHCH_2CH_2\cdot$$

44   **45**

(cyclopropyl, CH₃) CH=CHCOBu-t

46

R₂C=CHCH₂CH₂C(CH₃)₂CH=CHCOBu-t

47, R = H
48, R = CH₃

CH₂=CHCH₂C(CH₃)₂CH=CHCOBu-t

49

(cyclopropyl, CH₃)ĊH—CH=C(O⁻)Bu-t → ĊH₂CH₂C(CH₃)=CHCH=C(O⁻)Bu-t

50   **52**

CH₂=CHCH₂CH₂C(CH₃)₂ĊH—CH=C(O⁻)Bu-t →

51

(CH₃)₂(cyclopentyl)CH₂· ... CH=C(O⁻)Bu-t

53

half-lives for **50** and **51** being ca. 10^{-2} sec and 5 sec, respectively. These values, which correspond to the maximum rates for the rearrangements **50** → **52** and **51** → **53**, suggest that the rearrangement rates[24] for localized radicals **42** and **44** are each retarded by a factor of 10^6 or more when the radicals are delocalized in anion radicals **50** and **51**.

The reaction of each of the enones **46–49** with Me₂CuLi, with Li and t-BuOH in liquid NH₃, and with Cr(en)₂(OAc)₂ yielded only the normal products of conjugate addition or reduction such as **54** and **55**, and neither of the rearranged products **56** or **57** was detected.[11c] These results indicate that the lifetimes of radical anions in these reactions are less than 10^{-2} sec and, taken with the electrochemical data, indicate that radical cyclizations of the type **51** → **53** are too slow to be of value in intercepting anion radicals.

(cyclopropyl, CH₃)CH=CHCOBu-t

46

$$\xrightarrow[\substack{\text{or Li, }t\text{-BuOH in}\\ \text{liq. NH}_3}]{\text{Me}_2\text{CuLi in Et}_2\text{O} \quad \text{H}_2\text{O}}$$

(cyclopropyl, CH₃)CHCH₂COBu-t, R

54a, R = CH₃
b, R = H

CH₂=CHCH₂CH₂C(CH₃)₂CH=CHCOBu-t

47

$$\xrightarrow[\substack{\text{or Li, }t\text{-BuOH in}\\ \text{liq. NH}_3}]{\text{Me}_2\text{CuLi in Et}_2\text{O} \quad \text{H}_2\text{O}}$$

CH₂=CHCH₂CH₂C(CH₃)₂CHCH₂COBu-t, R

55a, R = CH₃
b, R = H

Although the reaction of the cyclopropyl enone **46** (Scheme VII) with Me₂CuLi parallels the behavior of

RCH₂CH₂C(CH₃)=CHCH₂COBu-t

56

(CH₃)₂(cyclopentyl, CH₂R)(CH₂COBu-t)

57

Scheme VII

(cyclopropyl, CH₃) CH=CHCOBu-t   ← 100% Me₂CuLi

46 ($E_{\text{red}} = -2.16$ V)

(cyclopropyl) CH=C(COEt)₂   ← 100% Me₂CuLi

58 (estimated[10] $E_{\text{red}} = -2.0$ V)

59 ($E_{\text{red}} = -2.25$ V)

60 (55% / 39% Me₂CuLi)

↓ Me₂CuLi

63 (half-life 10^{-3} sec) → **64**

↓   ↓

61 (43%)   **62** (49%)

65 ($E_{\text{red}} = -2.21$ V)   →ᵉ⁻

66 (half-life $<10^{-3}$ sec)

$$\xrightarrow[\text{liq. NH}_3]{\text{Li, EtOH}} \xrightarrow[\text{H}_2\text{CrO}_4]{\text{H}_2\text{O}}$$

67
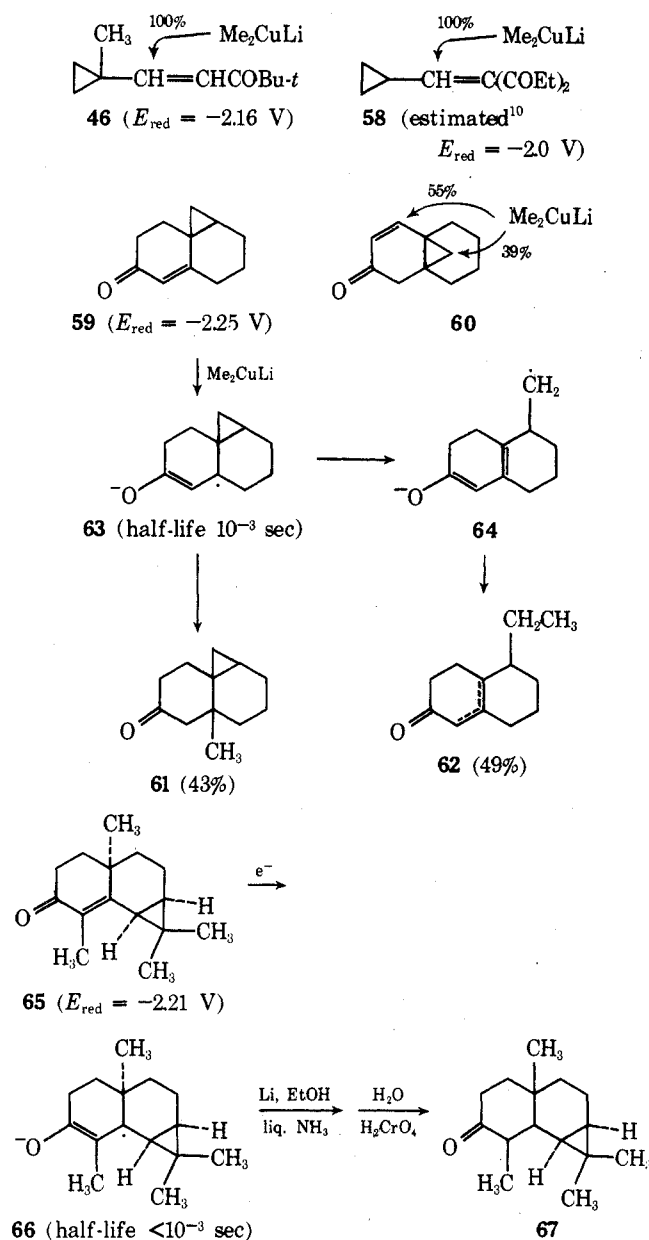
the cyclopropyl diester **58**[26] in forming only a normal conjugate adduct, two other cyclopropyl enones, **59** and **60**, do give mixtures of products from normal conjugate addition (e.g., **61**) and from rearrangement prior to addition (e.g., **62**).[27] The half-life of the anion radical **63** (from **59**) indicated that the rearrangement **63** → **64** was significantly faster than the rearrangement **50** → **52**,[11c] a result attributable to the more rigid geometry present in the anion radical **63** which holds a cyclopropane bond in an approximately perpendicular orientation to the plane of the enone system favoring ring opening. A similar enhanced rate of rearrangement was found in the anion radical **66** derived from the enone **65**[11c] which gives a

(26) P. A. Grieco and R. Findelhor, *J. Org. Chem.*, **38**, 2100 (1973).
(27) J. A. Marshall and R. A. Ruden, *J. Org. Chem.*, **37**, 659 (1972).

normal conjugate reduction product, **67,** with Li and EtOH in liquid NH_3.[28] These results suggest that the lifetime of the anion radical formed in reaction with Me_2CuLi is ca. 10^{-3} sec. Thus, cyclopropyl enones with appropriate E_{red} values are satisfactory substrates to detect radical-anion intermediates in cuprate additions provided that the rearrangement rate of the initially formed enone anion radical is ca. 10^3 sec^{-1} or greater. The results further indicate that the lifetime of the enone radical-anion intermediates formed in metal–NH_3 reductions is less than 10^{-3} sec and, taken with the earlier stereochemical isomerization results, suggests that the lifetimes of these intermediates are somewhere within the range 10^{-4} to 10^{-7} sec.

The foregoing comments concerning cyclopropyl carbonyl compounds would appear to be in disagreement with the recent observations[26,29] that lithium organocuprate reagents react slowly with each of the *nonenolizable esters* **68–70** to open the cyclopropane ring. However, consideration of both the very negative E_{red} values of these esters[11c] and the fact that each of the esters also reacts with diethyl sodiomalonate and other nucleophiles to form similar ring-opened products[30] indicates that these ring-opening reactions of esters **68–70** with cuprate reagents are examples of nucleophilic displacement reactions and do not involve an initial electron-transfer step. Additional evidence in support of this idea is gained from the fact that the cyclopropyl ketones **71** and **72** do not add Me_2CuLi[25,29a] in spite of the facts that the E_{red} values for these ketones[31] are less negative than the E_{red} values for esters **68–70** and that these ketones are reduced with ring opening when they are treated with a more powerful reducing agent, an alkali metal in liquid NH_3.[32]

68 ($E_{red} = -2.98$ V)

69 ($E_{red} = -2.93$ V)

70

71 ($E_{red} = -2.81$ V)

72 ($E_{red} = -2.88$ V)
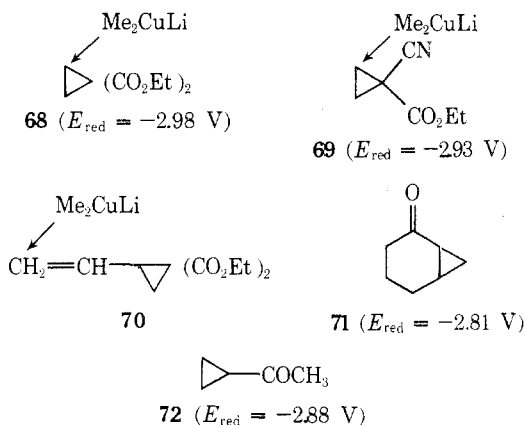
Finally, it is appropriate to note two recently published reactions of $Me_4Cu_2Li_2$ with unsaturated carbonyl compounds that are clearly compatible with an initial electron-transfer step to from an enone anion radical. Reaction of the enones **73**[33] and **74**[34] with $Me_4Cu_2Li_2$ failed to yield conjugate addition products. Instead, each of the anion-radical intermediates eliminated a relatively stable anion and was then further reduced[34b] to form the products **75** and **76**.
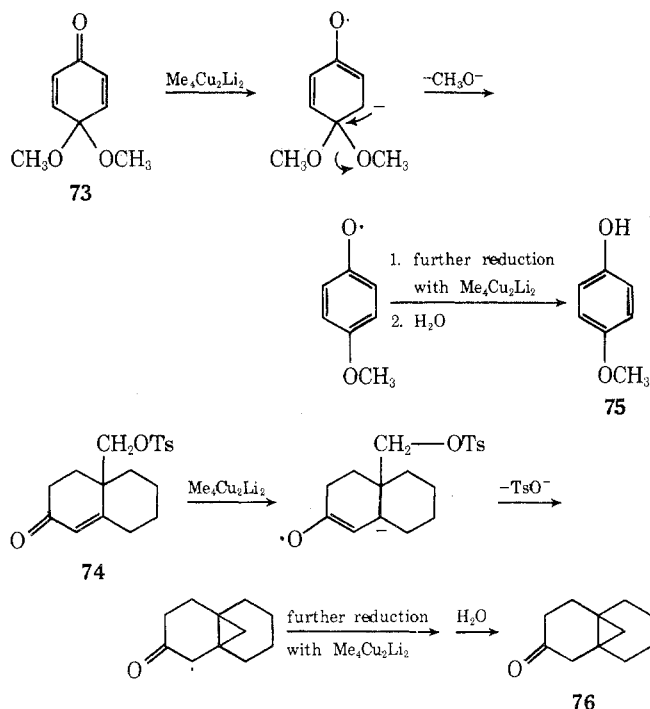
Summary

To predict whether an addition proceeding *via* an initial electron-transfer process rather than a direct nucleophilic addition is energetically favorable, the values $E_{red} - E_{ox}$ for the reaction under consideration are useful in any case where the E_{ox} value of the nucleophile, N:$^-$, can be estimated. In cases where the success or failure of a reaction can clearly be correlated with the value $E_{red} - E_{ox}$, this correlation provides rather compelling evidence that the reaction proceeds by an initial electron-transfer step. The correlation of product structure with the spin densities of radical intermediates such as **2** or **3** may provide circumstantial evidence for a process involving initial electron transfer, especially if the product structure can be shown to vary in a predictable way with the $E_{red} - E_{ox}$ value.

The use of cis → trans isomerization of certain enones appears to be one of the more sensitive methods (other than EPR spectrometry) to detect the presence of short-lived anion radicals in a reaction mixture. Unfortunately this observation of cis → trans isomerization, even when accompanied by appropriate control experiments, does not establish that the anion radicals are necessarily intermediates on the reaction path to products. The lack of stereochemical

(28) R. B. Bates, G. Büchi, T. Matsuura, and R. R. Shaffer, *J. Am. Chem. Soc.,* **82,** 2327 (1960).

(29) (a) G. Daviaud and Ph. Miginiac, *Tetrahedron Lett.,* 997 (1972); (b) R. D. Clark and C. H. Heathcock, *ibid.,* 529 (1975); (c) E. J. Corey and P. L. Fuchs, *J. Am. Chem. Soc.,* **94,** 4010 (1972).

(30) (a) E. D. Bergmann, D. Ginsberg, and R. Pappo, *Org. React.,* **10,** 205 (1959); (b) R. W. Kierstead, R. P. Linstead, and B. C. L. Weedon, *J. Chem. Soc.,* 3616 (1952); (c) J. M. Stewart and G. K. Pagenkopf, *J. Org. Chem.,* **34,** 1 (1969); (d) S. Danishefsky and G. Rovnyak, *ibid.,* **40,** 114 (1975); *J. Chem. Soc., Chem. Commun.,* 820 (1972); (e) S. Danishefsky, G. Rovnyak, and R. Cavanaugh, *J. Chem. Soc.,* 636 (1969); S. Danishefsky, M. Y. Tsai, and J. Dynak, *J. Chem. Soc., Chem. Commun.,* 7 (1975); (f) J. E. Dolfini, K. Menick, P. Corliss, R. Cavanaugh, S. Danishefsky, and S. Chakrabartty, *Tetrahedron Lett.,* 4421 (1966).

(31) H. O. House and A. V. Prabhu, to be published.

(32) S. W. Staley, *Sel. Org. Transform.,* **2,** 309 (1972).

(33) A. Nilsson and A. Ronlan, *Tetrahedron Lett.,* 1107 (1975).

(34) (a) D. J. Hannah and R. A. J. Smith, *Tetrahedron Lett.,* 187 (1975). (b) Although the authors formulated this reaction as an initial reduction of the enone **74** to its dianion, we believe that the very negative potentials (E_{red} more negative than ~3.0 V)[12a,b] that would be required to reduce a simple enone anion radical to the corresponding dianion makes this alternative very unlikely.

isomerization as evidence against an electron-transfer process is probably a more valid use of this test.

A test for an electron-transfer process based on the structural rearrangement of an initially formed anion radical appears to be useful with certain cyclopropyl enones. Provided the rate of rearrangement of the cyclopropyl ketone is sufficient, this experimental test offers compelling evidence for an anion-radical intermediate. Since this experimental probe also provides information about the lifetime of a radical-anion intermediate, hopefully a series of cyclopropyl ketones can be found whose anion radicals rearrange at significantly different rates. Finally, the use of an enone whose anion radical is capable of eliminating an anionic substituent also offers compelling evidence for the presence of an intermediate formed by initial electron transfer.

Magnetism and Magnetic Transitions of Transition-Metal Compounds at Low Temperatures

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A paramagnetic transition-metal compound contains ions with unpaired electron spins. It is attracted into a magnetic field, whereas diamagnetic compounds have filled shells and are repelled by a field. Quantitative measurement of this effect is convenient for diagnosis, since the degree of attraction into a field, the susceptibility, is proportional to the number of unpaired electrons. Thus, magnetic properties at high temperatures (that of liquid nitrogen and above) are often used in a subsidiary fashion in order to help characterize a transition-metal compound.

Paramagnetism is a single-ion effect in that, given the electronic structure of the constituents, the susceptibility may be calculated exactly by straightforward thermal averaging procedures.[1] The interactions between ions are negligible.

A simple model of a paramagnet suggests that the field aligns the spins parallel to it, while thermal agitation opposes this alignment, and leads[1] to the Curie law, which says the susceptibility is inversely proportional to temperature. The Hamiltonian used is the usual Zeeman one,

$$\mathcal{H} = g\mu_B S_z H_z \qquad (1)$$

where g is a splitting constant, characteristic of a given system, μ_B is the Bohr magneton, H_z is the magnitude of the field, and S_z is the usual spin operator. The Curie law is then found[1] as

$$\chi = \frac{Ng^2\mu_B^2 S(S+1)}{3kT} \qquad (2)$$

where N is Avogadro's constant, S is the spin of the ion, and k is the Boltzmann constant.

The magnetic susceptibility of a typical Curie law paramagnet, manganese Tutton salt, is illustrated in Figure 1a. This is the behavior typical of all isotropic materials at temperatures high with respect to any magnetic interactions, such as magnetic exchange, between the ions. Other substances, such as copper salts, obey the Curie law but with susceptibilities anisotropic because of g-value anisotropy. In order to observe this effect it is necessary to measure oriented single crystals, especially since there is more than one source of magnetic anisotropy, as we shall see.

A more important paramagnetic anisotropy arises when zero-field splittings occur,[1] that is, when the ground state may not be described only by the total spin, S. When the ground state of a system has spin degeneracy, such as with the $^3A_2$ state of vanadium(III), an axial distortion described by the spin Hamiltonian,

$$\mathcal{H} = D[S_z^2 - \tfrac{1}{3}S(S+1)] \qquad (3)$$

where D is the zero-field splitting parameter, can resolve the system into a doubly degenerate $m = \pm 1$ state, separated D/k in energy from the $m = 0$ state. Note that D/k not only has magnitude, but also sign.

As is illustrated in Figure 1b, at temperatures high with respect to D/k the susceptibilities are Curie-like, but susceptibilities measured parallel and perpendicular to the axis of quantization at temperatures comparable to D/k are different and quite unlike Curie behavior. A representative system with be-

(1) R. L. Carlin, *J. Chem. Educ.*, **43**, 521 (1966).