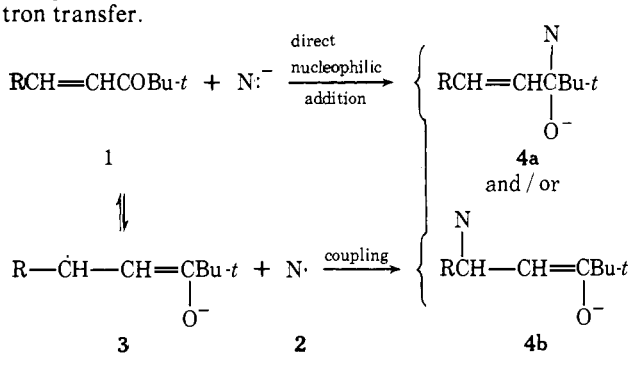
Reactions Involving Electron Transfer. VII. Use of Intramolecular Reactions as a Test for Anion Radical Intermediates[1]

Herbert O. House* and Paul D. Weeks

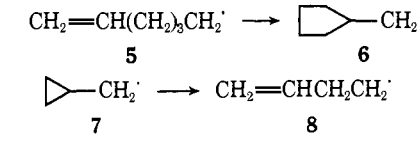
Contribution from the School of Chemistry, Georgia Institute of Technology, Atlanta, Georgia 30332. *Received November 1, 1974*

Abstract: The unsaturated carbonyl compounds **9–13** have been prepared and studied as examples of enone systems **1** in which the group R is a potential intramolecular "trap" for anion radical intermediates **3.** The anion radicals derived from the alkenyl enones **9–12** proved to be usually stable; consequently, use of these enones in reactions [addition of $(CH_3)_2CuLi$, reduction with $Cr(en)_2(OAc)_2$, reduction with Li in $NH_3(l)$] thought to involve ion radical intermediates led only to normal, acyclic products (Scheme II). Appropriate control experiments suggest that the slow rate of cyclization is not attributable to steric interference. The cyclopropyl anion radical **21** (derived from **13**) rearranged more rapidly but still the rate of rearrangement (i.e., **40** → **41**) was not sufficiently rapid to detect radical anion intermediates in either the addition of $(CH_3)_2CuLi$ or reduction with Li in $NH_3(l)$. Comparison of the stabilities of anion radicals derived from several cyclopropyl enones **13**, **30**, **31**, and **33** indicates that a rearrangement rate (**40** → **41**) of about 10^3 sec^{-1} is required for a cyclopropyl enone in order to detect the radical ion intermediates present in $(CH_3)_2CuLi$ addition and suggests that the rearrangement rate $>10^4$ sec^{-1} would be required to detect the radical ion intermediate in metal–$NH_3(l)$ reductions.

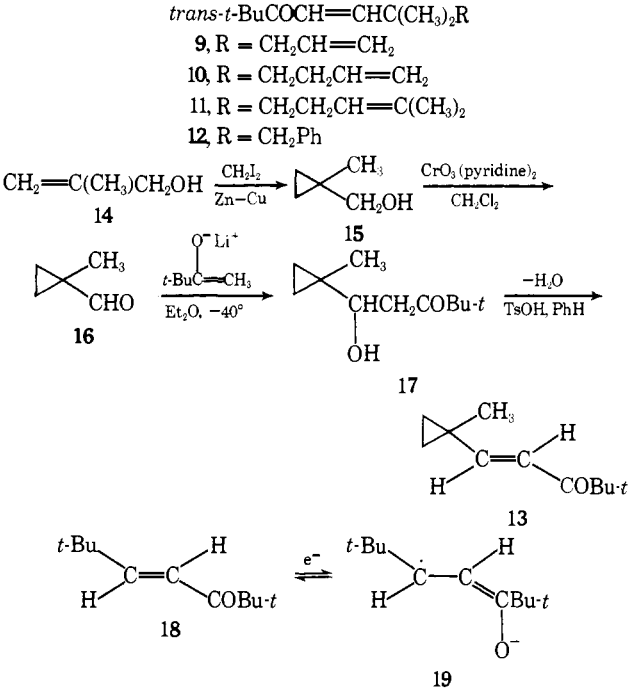
An accompanying paper[2a] describes our exploration of a stereochemical test to distinguish between reactions of an unsaturated carbonyl compound **1** and a nucleophile, $N:^-$, that proceed by direct nucleophilic attack and reactions that involve initial electron transfer to form ion radical (or radical) intermediates **2** and **3** prior to formation of the product(s) **4.** Although this stereochemical test appears capable of detecting anion radicals **3** in reaction mixtures provided they have *minimum lifetimes* somewhere within the range 10^{-4} to 10^{-7} sec, the method does not distinguish between the possibilities that the anion radical **3** is an intermediate on the reaction path to form product **4** rather than a by-product present in equilibrium with the starting enone **1,** but not a direct precursor for the product **4.** In an effort to find a different experimental probe bearing on this question, we report here a study of several enones **1** that contain substituents R offering the possibility of detecting the initially formed anion radical **3** by the occurrence of an intramolecular *structural rearrangement* prior to coupling. If this intramolecular *structural rearrangement* of **3** were to occur more rapidly than coupling of **2** and **3,** then products *structurally isomeric* with **4** should be observed in a reaction proceeding by a two-step process involving initial electron transfer.



The two intramolecular processes that we selected for this study are based upon the known cyclization of hexenyl radicals **5** to cyclopentylcarbinyl radicals **6** (rate constant ca. 10^5 sec^{-1})[3,4] and the known opening of cyclopropylcarbinyl radicals **7** to form 3-butenyl radicals **8** (rate constant ca. 10^8 sec^{-1}).[4] We expected the rates of these intramolecular processes, cited for unstabilized radicals, to be diminished when the radicals involved were stabilized by incorporation in an anion radical system **3** (or the analogous allylic radicals formed by association of **3** with a proton or a metal cation). However, the magnitude of this rate retardation was uncertain at the outset of this study. The systems selected for study included the γ-alkenyl-α,β-unsaturated ketones **9–12** (see Scheme I) whose preparations were described elsewhere[5] and the cyclopropyl-substituted enone **13** that was obtained by the aldol condensation[6] of the aldehyde **16** with the lithium enolate of pinacolone followed by dehydration of the ketol **17.** These particular α,β-unsatu-



Scheme I



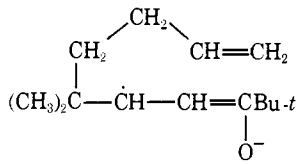
rated ketones **9–13** were chosen because they lacked relatively acidic C–H bonds at the γ and α' positions which would contribute to instability of the corresponding anion radicals.[7] Thus, except for the presence of a potentially reactive alkenyl group or a cyclopropane ring as a γ substituent, each of these enones **9–13** is analogous to the enone **18** that could be reduced ($E_{1/2}$ = −2.207 V vs. SCE) to the anion radical **19**.[7] This anion radical **19** is relatively stable in an oxygen-free DMF solution, decaying by a pseudo-first-order process (proton abstraction from the solvent or supporting electrolyte followed by dimerization) with a half-life of ca. 20 min at 25°.[7a,8]

Table I. Electrochemical Reduction of Enones at 25° in DMF Solution Containing 0.5 *M* *n*-Bu_4NBF_4

Enone (concn, $M \times 10^{-3}$)	Polarography			Cyclic voltammetry	
	$E_{1/2}$, V vs. SCE	n	i_d, μA	$E_{1/2}$, V vs. SCE	Half-life, sec
9 (3.4–4.7)	−2.18	1.1	17–19	−2.26	>10[a]
10 (4.2–4.6)	−2.19	1.0	17–22	−2.22	5
11 (2.3–3.0)	−2.20	1.2	10–12	−2.19	>10[b]
12 (4.1–5.4)	−2.19	1.0	16–20	−2.21	>10
13 (4.8–5.1)	−2.16	0.9	22–24	−2.25	10^{-2}[c]
18 (8.0–8.3)	−2.205 (−2.207)[d]	1.0	32–35	−2.22	>10[d,e]
30 (6.4–7.0)	−2.21	0.9	21–23	ca. −2.2	$<10^{-3}$
31 (4.6–5.0)	−2.10	1.4	17–18	ca. −2.1	$<10^{-3}$
33 (6.0–7.0)	−2.25	0.9	30–36	−2.26	10^{-3}

[a] The presence of 0.5 *M* H_2O in the solution shortened the half-life to ca. 2 sec. [b] The presence of 0.3 *M* H_2O in the solution shortened the half-life to 5 sec. [c] Similar values were obtained with solutions that were 0.0006, 0.0023, and 0.006 *M* in the enone 13. [d] Data from ref 7a. [e] The presence of 0.5 *M* H_2O in the solution shortened the half-life to 0.4 sec. The value of this half-life in an anhydrous solution was determined to be 21 min by following the decay of absorption at 450 mμ with a spectrophotometer (cf. ref 7a).

The electrochemical reduction of each of the enones **9–13** in DMF solution containing 0.5 *M* *n*-Bu_4NBF_4 was examined by polarography (dropping Hg electrode) and by cyclic voltammetry (stationary Hg-coated Pt electrode). The results of these measurements are presented in Table I which includes, for comparison, the analogous data for enone **18.** It will be noted that the reduction potentials for all of these enones are very similar ($E_{1/2}$ = 2.18 ± 0.03 V vs. SCE) indicating that the various γ substituents do not facilitate addition of an extra electron to the enone system. Of more interest to this study was the finding that the radical anions (e.g., **20**) derived from the enones **9–11** with γ-alkenyl substituents were remarkably stable with half-lives of the order of 10 sec or greater. Even the enone **13** with a cyclopropyl substituent exhibited reversible behavior upon reduction at rapid scan rates allowing us to estimate a half-life of ca. 10^{-2} sec for the radical anion **21.** Thus, the rates of rearrangement of these radical anions **20** and **21** are at least 10^6 times slower than the unstabilized radicals **5** and **7**.[9] As a consequence, it was apparent that utilization of these enones (especially enones **9–12**) to detect the presence of intermediates such as **3** by structural rearrangement would only be successful if the recombination of these intermediates (**2** + **3** → **4**) was a relatively slow process.



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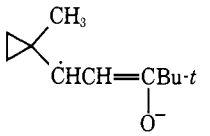

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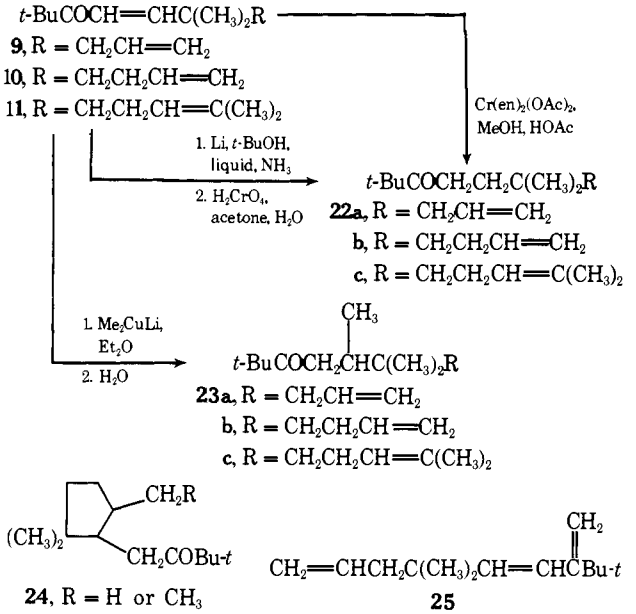
Scheme II

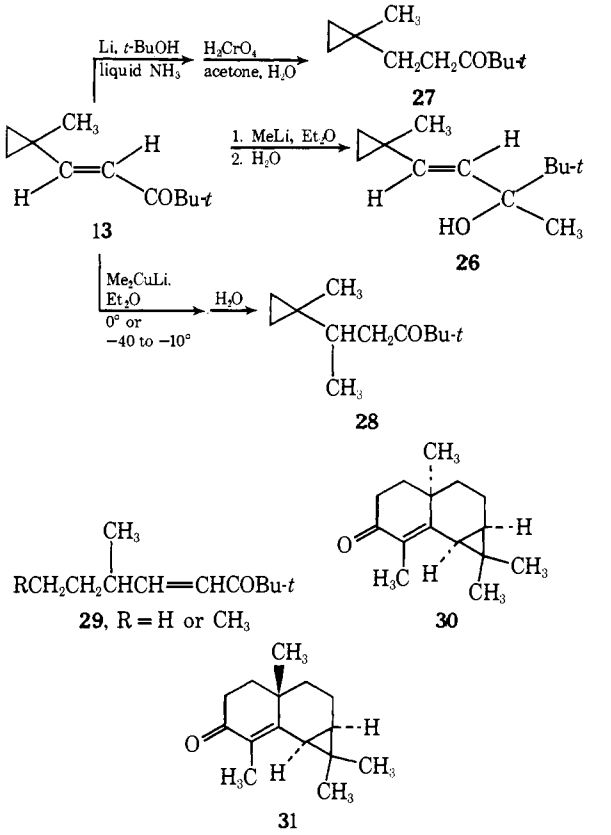


24, R = H or CH_3

25

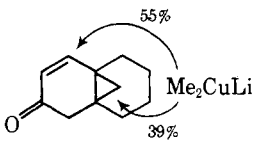
To investigate the possibility, each of the γ-alkenyl enones **9–11** was subjected to three reactions believed[2a] to involve the formation of radical or radical ion intermediates (Scheme II), namely, reduction with Li and *t*-BuOH in liquid NH_3,[7] reduction with the chromium(II) complex, $Cr(en)_2(OAc)_2$,[10] and addition of Me_2CuLi.[11] As indicated in Scheme II, each of these reactions proceeded without rearrangement yielding the "expected" conjugate reduction or addition products **22** and **23** with no evidence for the formation of rearranged products such as **24** (from cyclization of **20**). We, therefore, concluded that any radical or anion radical intermediates (e.g., **20**) underwent coupling or further reduction much more rapidly than the intermediates cyclized.

Scheme III



We turned our attention to the cyclopropyl enone **13,** examining the addition of MeLi (believed not to involve initial electron transfer)[2a] and reactions with Me_2CuLi and with Li and *t*-BuOH (both believed to involve initial electron transfer).[2a,7,11] As indicated in Scheme III, all of these reactions also yielded the "expected" products **26, 27,** and **28** with no evidence for the formation of products such as **29** in which the cyclopropane ring had been opened. The absence of such ring-opened products in the metal–NH_3 reduction was not unexpected since, as noted previously,[2a] the lifetime of intermediate radicals (or anion radicals) in metal–NH_3 reductions appears to be much shorter than the measured half-life (ca. 10^{-2} sec) for the radical anion **21.** This observation is in agreement with studies of the metal–NH_3 reduction of other cyclopropyl enone systems such as **30** and **31** in which saturation of the C–C double bond without ring opening has been observed.[12]

The results to be expected from reaction of the cyclopropyl enone **13** with Me_2CuLi were less certain. In reactions of Me_2CuLi with the ketones **32** and **33,** both the products



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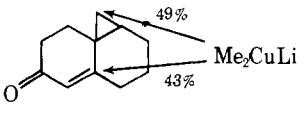

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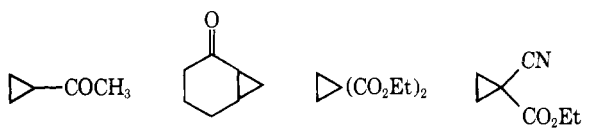
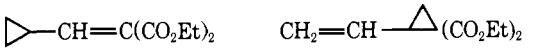
of normal conjugated addition (analogous to **28**) and products derived from opening of the cyclopropane ring (analogous to **29,** R = CH_3) were found.[13a] Simple cyclopropyl ketones such as **34**[13b] and **35**[13a,c] failed to react with Me_2CuLi but the corresponding malonates such as **36**[13b,d] and the cyanoacetate **37**[13d] were found to react with



34 **35** **36** **37**

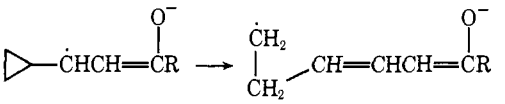
Me_2CuLi to give ring-opened products. The conjugated diester **38**[13e] gave only the normal conjugated addition product (analogous to **28**) but reaction of Me_2CuLi with the isomeric diester **39**[13e] resulted in addition to the C–C



38 **39**

double bond with opening of the cyclopropane ring. Although these various reactions of cyclopropane derivatives might appear to be related, we believe that the reactions of the various *nonconjugated* malonic acid derivatives **36, 37,** and **39** with cuprate reagents are proceeding by a mechanism quite different from the *conjugated* derivatives **13, 32, 33,** and **38.** Whereas all of the conjugated derivatives can be expected[14] to be reduced at potentials less negative than −2.4 V (vs. SCE), the apparent maximum for transfer of an electron from Me_2CuLi,[11] we find the reduction potential for the malonate **36** (ca. −2.98 V vs. SCE, the value for the malonate **39** is presumably similar) and the cyanoacetate **37** (ca. −2.93 V vs. SCE) to be much more negative and well beyond the range where electron transfer from Me_2CuLi would be expected. We are led to believe that the reactions of the esters **36, 37, 39,** and related systems do not involve an initial electron-transfer process but instead proceed by a nucleophilic displacement reaction unrelated to the usual conjugate addition of cuprate reagents to enones. In fact, there is ample precedent for this idea in early observations that each of the *nonconjugated* esters **36, 37,** and **39** reacts with the anion of diethyl malonate or ethyl cyanoacetate to give products analogous to those obtained with cuprate reagents.[15] The oxidation potential for the anion of diethyl malonate ($E_{1/2}$ = +0.4 V vs. SCE)[2b] is much too positive for this material to transfer an electron to these *nonconjugated* esters.

Among the *conjugated* systems, the question remains as to why two of the compounds **13** and **38** react with Me_2CuLi to give only normal conjugate addition products (analogous to **28**) whereas the other two compounds **32** and **33** react in part to give products analogous to **29** in which opening of the cyclopropyl ring has occurred. In considering these results we were led to wonder if the distinction between these reactions was simply a reflection of the relative rates of rearrangement **40** → **41** of the radical ions **40** involved. In particular, with relatively rigid systems such as **30–33** where one of the cyclopropyl C–C bonds is held approximately perpendicular to the plane of the enone system, one might expect the rearrangement **40** → **41** to be facilitated. To explore this idea, the stabilities of the anion radicals derived from enones **30, 31,** and **33** were studied by cyclic voltammetry (see Table I).[16] The half-life of each of these radical ions was found to be ca. 10^{-3} sec or less, the limit of our measurements. Thus, the rearrangement **40** → **41** of radical anions from enones **30, 31,** and **33** is about ten times more rapid than the corresponding rearrangement of the radical anion from enone **13.** Since Me_2CuLi adds to the enone **13** without rearrangement and adds with only partial rearrangement to the enone **33,** we estimate that the half-lives of intermediates **2** and **3** in these cuprate–enone reactions are in the range of 10^{-3} sec.

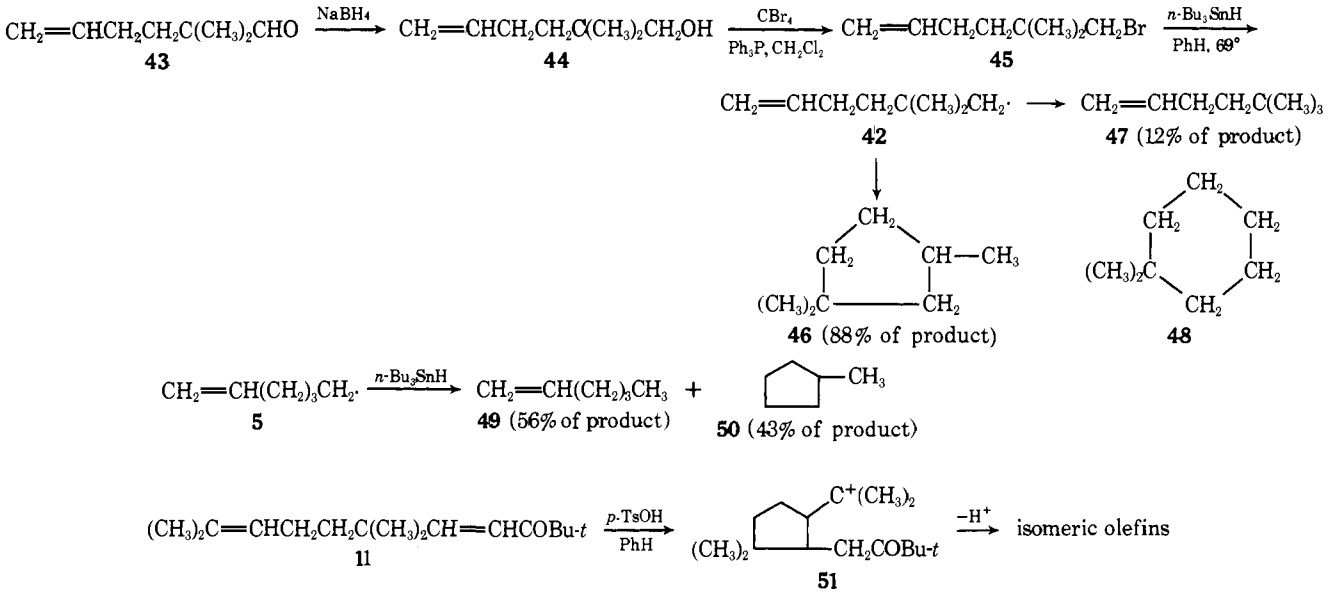


40 **41**

The results of this study and earlier publications[13] indicate that enones with β-cyclopropyl substituents may sometimes be used to detect anion radical intermediates **40** by finding products derived from the rearranged anion radicals **41.** The most serious limitation of this experimental test is the relatively slow rate of the rearrangement **40** → **41** so that only electron-transfer reactions which involve relatively long-lived intermediates **2** and **3** will produce rearranged products. Thus, it appears unlikely that the rather short-lived intermediates formed in the reduction of enones with alkali metals in ammonia[2a] will be detected by this method.[17] We are continuing to examine other cyclopropyl enones in an effort to find structures that will undergo the rearrangement **40** → **41** more rapidly than anion radicals derived from enones **30–33.**

The rates of rearrangement of the anion radicals, such as **20,** derived from the γ-alkenyl enones **9–11** are sufficiently slow that we believe reactions with these enones will be of little value as a test for radical anion intermediates. The slow rate of rearrangement of anion radicals, such as **20,** would appear to be adequately explained by delocalization in the anion radical. However, to explore the possibility that the rather slow reaction of anion radical **20** might be attributable to steric interference by the gem dimethyl group, we have examined the behavior of the similarly substituted hexenyl radical **42** (Scheme IV). In other studies of the effect of substituents on the rate of cyclization of the hexenyl radical **5**,[18a-c] substituents at C-1 or C-6 have relatively little effect on the rate of cyclization **5** → **6** but this reaction is

Scheme IV



retarded by the presence of substituents at C-5. Substituents at C-2 (analogous to the substitution in radical **42**) have been suggested[18c] to be responsible for low yields of cyclized products in other cases.

The previously described[5] aldehyde **43** was converted (Scheme IV) to the bromide **45** whose reaction with *n*-Bu_3SnH was used to generate the radical **42.** For this reaction we employed a PhH solution that was ca. 0.5 *M* in bromide and ca. 0.5 *M* in *n*-Bu_3SnH with a reaction temperature of 69°. The products, formed in 82% yield, were the cyclopentane **46** (88% of the product) and the olefin **47** (12% of the product); none of the cyclohexane **48** was detected. In an earlier study[18a] where the unsubstituted hexenyl radical **5** was generated employing essentially the same reaction conditions, the products were the olefin **49** (56% of the product) and the cyclopentane **50** (43% of the product). Since the reactions of radicals **42** and **5** with *n*-Bu_3SnH to form olefins **47** and **49** are expected to be very similar in rate,[18a] we conclude that the gem dimethyl group in the radical **42** enhances the rate of cyclization to form the radical precursor of cyclopentane **46.** This rate of enhancement is presumably another example of the Thorpe-Ingold effect.[18d] An additional indication of the ease of ring closure in these systems was obtained in the previously reported[5] facile acid-catalyzed cyclization of the enone **11** to form a mixture of olefins derived from the carbonium ion **51.** Consequently, all of our data indicate that the very slow rate of cyclization of the anion radicals such as **20** is best attributed to delocalization of spin density in the starting radical.

Experimental Section[19]

Preparation of the Ketol 17. Following a previously described procedure,[20] 17.0 g (0.22 mol) of the alcohol **14** was treated with the reagent from 160 g (0.60 mol) of CH_2I_2 and 44 g of dry Zn-Cu[21] to form the cyclopropylcarbinol **15** as a colorless liquid: bp 122–129°; $n^{25}D$ 1.4290–1.4331 [lit.[22] bp 125.8–126.3° (739 mm); $n^{25}D$ 1.4290–1.4292]; yield 12.35 g (65%); ir (CCl_4), 3620, 3600, 3440 (OH), and 3070 cm^{-1} (cyclopropyl CH); NMR (CCl_4) δ 4.45 (1 H, broad, OH), 3.2–3.5 (2 H, m, CH_2O), 1.10 (3 H, s, CH_3), and 0.1–0.6 (4 H, m, cyclopropyl CH_2). A 12.0-g (140-mmol) sample of the alcohol **15** was oxidized with Collins' reagent[23] [prepared in situ[24] at 0° from 158 g (2.00 mol) of pyridine, 100 g (1.00 mol) of CrO_3, and 2000 ml of CH_2Cl_2]. After the reaction mixture had been stirred at 25° for 15 min, the solution was decanted and the Cr-salt residue[25] was washed with Et_2O. The combined organic solutions were washed successively with aqueous 5% NaOH, aqueous 5% HCl, aqueous $CuSO_4$, aqueous 5% HCl, aqueous $NaHCO_3$, and aqueous NaCl and then dried and concentrated. Distillation of the residue separated 5.81 g (49%) of the aldehyde **16** as a colorless liquid: bp 103–108°; $n^{25}D$ 1.4264–1.4281 (lit.[26] bp 103–109°; $n^{25}D$ 1.4251); ir (CCl_4), 3070 (cyclopropyl CH), 2705, 2770, 2805 (aldehyde CH), and 1720 cm^{-1} (C=O); NMR (CCl_4) δ 8.61 (1 H, s, CHO), 1.18 (3 H, s, CH_3), and 0.8–1.2 (4 H, m, cyclopropyl CH_2).

To a cold (−40°) solution of *i*-Pr_2NLi, from 5.0 g (50 mmol) of *i*-Pr_2NH and 48 mmol of MeLi in 126 ml of Et_2O, was added, dropwise and with stirring during 5 min, 4.80 g (48 mmol) of pinacolone. After the resulting solution had been stirred at −40° for 30 min, a solution of 4.07 g (48 mmol) of the aldehyde **16** in 15 ml of Et_2O was added, dropwise and with stirring. The resulting solution was stirred at −40° for 15 min and poured into cold aqueous 1 *M* HCl and extracted with Et_2O. The ethereal extract was washed successively with aqueous $NaHCO_3$ and with aqueous NaCl and then dried and concentrated to leave 6.51 g (74%) of the crude ketol **17** as a low-melting solid. Sublimation (70° at 1 mm) separated 5.54 g (63%) of the ketol **17**, mp 44–46°. Recrystallization of the ketol from hexane at Dry Ice temperature followed by an additional sublimation (70° at 0.02 mm) afforded the pure ketol **17** as white plates: mp 48–49°; ir (CCl_4) 3520 (broad, OH), 3070 (cyclopropyl CH), and 1695 cm^{-1} (C=O); NMR ($CDCl_3$) δ 3.2–3.6 (1 H, m, carbinol CH), 2.98 (1 H, broad, OH, exchanged with D_2O), 2.5–2.9 (2 H, m, CH_2CO), 1.13 (9 H, s, *t*-Bu), 1.06 (3 H, s, CH_3), and 0.2–0.6 (4 H, m, cyclopropyl CH_2); mass spectrum, m/e (rel intensity) 138 (13), 123 (79), 109 (88), 100 (50), 84 (25), 83 (32), 81 (58), 57 (100), 56 (38), 55 (62), 53 (31), 43 (62), 41 (65), and 39 (43).

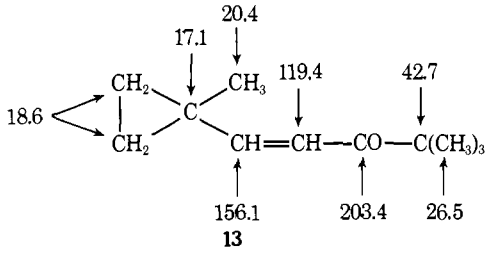
Anal. Calcd for $C_{11}H_{20}O_2$: C, 71.69; H, 10.94. Found: C, 71.74; H, 10.94.

Preparation of the Enone 13. A solution of 4.5 g (24 mmol) of the ketol **17** and 61 mg of *p*-TsOH in 200 ml of PhH was refluxed for 10 min. The solution was cooled, diluted with Et_2O, washed successively with aqueous $NaHCO_3$ and with aqueous NaCl, and then dried and concentrated. The residual crude liquid enone **13** was distilled in a short-path still to separate 2.85 g (72%) of colorless liquid fractions (bp 70–110° (15–22 mm); $n^{25}D$ 1.4557–1.4750) that contained (GLC, Carbowax 20 *M* on Chromosorb P) mainly the enone **13** (ret time 14.0 min) accompanied by a more volatile impurity (2.8 min). The residue from the distillation (355 mg) also contained (GLC) mainly the enone **13.** The crude product was sublimed (50° at 1 mm) onto a cold (Dry Ice and acetone) surface to separate 2.49 g (63%) of the pure enone **13** as a solid that melted to a colorless liquid, $n^{25}D$ 1.4755, as it warmed to room temperature: ir (CCl_4) 3075, 3055 (cyclopropyl CH), 1685 (conjugated C=O), 1612 (conjugated C=C), 985, and 930 cm^{-1} (*trans*-CH=CH); uv maxima (95% EtOH) 256 (ϵ 7300) and 326 mμ (inflection, ϵ 60); NMR (CCl_4) δ 6.33 (2 H, s, vinyl CH), 1.17 (3 H, s, CH_3), 1.04 (9 H, s, *t*-Bu), and 0.6–0.9 (4 H, m, cyclopropyl CH_2); mass spectrum, *m/e* (rel intensity) 166 (M^+, <1), 109

(100), 81 (69), 57 (16), and 41 (18).

Anal. Calcd for $C_{11}H_{18}O$: C, 79.46; H, 10.92. Found: C, 79.46; H, 10.94.

The natural abundance of the ^{13}C NMR spectrum of the enone **13**, measured in $CDCl_3$ solution with added TMS, is summarized in the following structure. The chemical shift assignments, indicated in ppm, were verified by off-resonance decoupling measurements.



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Electrochemical Measurements. The polarographic and cyclic voltammetry measurements employed a custom-made polarographic module utilizing solid-state amplifiers that followed by typical three-electrode design. Descriptions of the cells, working electrodes, reference electrodes, and reagent purification procedures have been published previously.[10,27] The procedures used to estimate $E_{1/2}$ values and half-lives from cyclic voltammetry measurements are those described previously.[7a,27] The values obtained from these measurements are summarized in Table I. Approximate $E_{1/2}$ values for the cyclopropane esters **36** and **37** were obtained by polarographic measurement in DMF containing 0.5 *M* n-Bu_4NBF_4. Since the reduction waves for these compounds were almost as negative as the discharge potential for the electrolyte, the $E_{1/2}$ values obtained are only approximate.

To obtain a sample of the enone **33** for electrochemical measurement, a previously described procedure[28] was used to convert 6-methoxy-1-tetralone to 2-keto-$\Delta^{1,10},\Delta^{8,9}$-hexahydronaphthalene. Reaction of 1.57 g (10.6 mmol) of this dienone with the ylid, from 3.7 g (16.7 mmol) of $Me_3SO^+I^-$ and 635 mg (15.1 mmol) of NaH, in 15 ml of DMSO as previously described[13a] yielded, after short-path distillation, 1.03 g of crude liquid product, $n^{25}D$ 1.5477. A 816-mg aliquot of this material was purified by preparative TLC [silica gel, E. Merck F 254, with a 1:3 (v/v) Et_2O–hexane mixture as eluent] to separate 660 mg (corresponding to a 48% yield) of the desired enone **33** (R_f 0.63). A pure sample of the enone **33** was collected (GLC) as a colorless liquid: $n^{25}D$ 1.5527 [lit.[13a] bp 90° (0.2 mm)]; ir (CCl_4) 1667 (conjugated C=O) and 1607 cm^{-1} (conjugated C=C); uv max (95% EtOH) 267 mμ (ε 14,100); NMR (CCl_4) δ 5.7–5.8 (1 H, m, vinyl CH) and 0.7–2.6 (13 H, m, aliphatic CH); mass spectrum, *m/e* (rel intensity) 162 (M^+, 100), 134 (37), 120 (51), 119 (29), 105 (41), 92 (25), 91 (59), and 39 (25). Anal. Calcd for $C_{11}H_{14}O$: 162.1045. Found: 162.1054. This material was identified with the previously described sample[13a] by comparison of ir spectra.[29] The enones **30** and **31**[16] have the following uv maxima (95% EtOH):**30**, 266 mμ (ε 13,700); **31**, 279 mμ (ε 15,500).

Reductions with Li and *t*-BuOH in liquid NH_3. A. The Dienone 10. To a cold (−78°) solution of 0.26 g (37 mg-atom) of Li in 50 ml of NH_3 (distilled from Na) was added a solution of 385 mg (1.85 mmol) of the dienone **10** and 163 mg (2.2 mmol) of *t*-BuOH in 10 ml of Et_2O. After the resulting solution had been stirred at −78° for 5 min, excess solid NH_4Cl was added and the NH_3 was allowed to evaporate. The residue was partitioned between Et_2O and aqueous NaCl and the Et_2O layer was dried and concentrated. After a cold (0°) solution of the crude organic product in 10 ml of acetone had been treated with 2.0 ml of aqueous 8 *N* H_2CrO_4 and stirred for 5 min at 0°, 1.0 ml of isopropyl alcohol was added. The resulting mixture was partitioned between Et_2O and aqueous NaCl and the Et_2O layer was dried and concentrated to leave 300 mg (77%) of the crude ketone **22b** (NMR analysis) which exhibited a single GLC peak (retention time 15.2 min) on a column (Apiezon L on Chromosorb P) where the retention time of the starting dienone **10** was 13.2 min. A collected (GPC) sample of the pure ketone **22b** was obtained as a colorless liquid: $n^{25}D$ 1.4441; ir (CCl_4) 1705 (C=O), 1640 (C=C), 1002, and 921 cm^{-1} (CH=CH_2); NMR (CCl_4) δ 5.4–6.1 (1 H, m, vinyl CH), 4.7–5.2 (2 H, m, vinyl CH), 1.2–2.6 (8 H, m, aliphatic CH), 1.11 (**9** H, s, *t*-Bu), and 0.87 (6 H, s, CH_3); mass spectrum, *m/e* (rel intensity) 210 (M^+, <1), 194 (3), 152 (34), 69 (67), 57 (100), 55 (50), 43 (40), and 41 (50).

Anal. Calcd for $C_{14}H_{26}O$: C, 79.93; H, 12.46. Found: C, 80.01; H, 12.47.

B. The Dienone 9. The same reduction procedure was applied to 377 mg (1.94 mmol) of the dienone **9** to give 273 mg (72%) of the crude ketone **22a** (ir analysis). This product exhibited a single GLC peak (retention time 16.3 min) on a column (Apiezon L on Chromosorb P) where the retention time of the dienone **9** was 14.7 min. A collected (GLC) sample of the pure ketone **22a** was obtained as a colorless liquid: $n^{25}D$ 1.4418; ir (CCl_4) 1705 (C=O), 1635 (C=C), 1000, and 925 cm^{-1} (CH=CH_2); NMR (CCl_4) δ 5.4–6.2 (1 H, m, vinyl CH), 4.7–5.2 (2 H, m, vinyl CH), 1.2–2.6 (6 H, m, aliphatic CH), 1.06 (9 H, s, *t*-Bu), and 0.84 (6 H, s, CH_3); mass spectrum, *m/e* (rel intensity) 196 (M^+, 4), 181 (1), 155 (29), 139 (23), 97 (18), 69 (80), 57 (100), 55 (31), 43 (26), and 41 (47).

Anal. Calcd for $C_{13}H_{24}O$: C, 79.53; H, 12.32. Found: C, 79.46; H, 12.42.

C. The Dienone 11. Application of the same reduction procedure to 136 mg (0.57 mmol) of the dienone **11** gave 111 mg (82%) of the crude ketone **22c** (NMR analysis). This product exhibited a single GLC peak (ret time 17.6 min) on a column (Carbowax 20 *M* on Chromosorb P) when the retention time for the dienone **11** was 16.2 min. A collected (GLC) sample of the pure ketone **22c** was obtained as a colorless liquid: $n^{25}D$ 1.4527; ir (CCl_4) 1705 cm^{-1} (C=O); NMR (CCl_4) δ 5.06 (1, H, t, J = 6 Hz, vinyl CH), 1.2–2.6 (6 H, m, aliphatic CH), 1.60, 1.68 (6 H, broad singlets, allylic CH_3), 1.10 (9 H, s, *t*-Bu), and 0.87 (6 H, s, CH_3); mass spectrum, *m/e* (rel intensity) 238 (M^+, <1), 222 (1), 180 (41), 122 (20), 96 (31), 82 (24), 80 (43), 68 (100), 55 (71), 53 (25), 43 (61), and 41 (62).

Anal. Calcd for $C_{16}H_{30}O$: C, 80.60; H, 12.68. Found: C, 80.76; H, 12.71.

Addition of Me_2CuLi. A. To Dienone 10. To a cold (0°) solution of Me_2CuLi, from 314 mg (1.65 mmol) of purified[30] CuI and 3.2 mmol of halide-free MeLi (Foote Mineral Co.) in 10 ml of Et_2O, was added, dropwise and with stirring during 5 min, a solution of 302 mg (1.45 mmol) of the dienone **10** in 10 ml of Et_2O. The resulting mixture was stirred at 0° for 1 hr and then treated with aqueous NH_4Cl. The organic layer was removed and the aqueous phase was saturated with NaCl and extracted with Et_2O. The combined ethereal solutions were washed with aqueous NaCl, dried, and concentrated to leave 305 mg of crude product containing (NMR analysis and GLC analysis, Carbowax 20 *M* on Chromosorb P) the dienone **10** (ret time 13.2 min) and the ketone **23b** (15.4 min). Preparative thin-layer chromatography of this material on silica gel (Merck PF-254), with a 3:97 (v/v) Et_2O–hexane eluent, separated 234 mg (72%) of the ketone **23b** (R_f 0.50) and 67 mg (22%) of the starting dienone **10** (R_f 0.42) identified with an authentic sample by comparison of ir spectra and GLC retention times. A pure sample of the ketone **23b** was collected (GLC, Carbowax 20 *M* on Chromosorb P) as a colorless liquid: $n^{25}D$ 1.4508; ir (CCl_4) 1705 (C=O), 1640 (C=C), 1000, and 920 cm^{-1} (CH=CH_2); NMR (CCl_4) δ 5.3–6.1 (1 H, m, vinyl CH), 4.7–5.2 (2 H, m, vinyl CH), 1.1–2.5 (7 H, m, aliphatic CH), 1.09 (9 H, s, *t*-Bu), 0.83 (6 H, s, CH_3), and 0.74 (3 H, d, J = 7 Hz; CH_3); mass spectrum, *m/e* (rel intensity) 224 (M^+, <1), 167 (11), 127 (22), 111 (34), 109 (20), 83 (23), 69 (41), 57 (100), 55 (50), and 41 (39).

Anal. Calcd for $C_{15}H_{28}O$: C, 80.29; H, 12.58. Found: C, 80.53; H, 12.71.

B. To Dienone 9. The same reaction procedure was followed with 2.45 mmol of Me_2CuLi and 505 mg (2.6 mmol) of dienone **9** in 20 ml of Et_2O to yield 516 mg of a crude product that contained (ir and NMR analysis and GLC, Apiezon L on Chromosorb P) the ketone **23a** (ca. 70%, ret time 22.4 min), the starting dienone **9** (ca. 13%, 15.6 min), and an additional product (ca. 17%, 11.2 min) believed to be the triene **25** derived from dehydration of a 1,2-addition product (ir 3610 and 3570 cm^{-1} in crude product) during GLC collection. A collected (GLC) sample of this component, believed to be triene **25**, exhibited ir absorption (CCl_4) at 1640 (C=C) and 1615 cm^{-1} (conjugated C=C) with no absorption in the 3- or 6-μ region attributable to OH or C=O functions: mass spectrum, *m/e* (rel intensity) 192 (M^+ for **25**, 2), 151 (48), 109

(45), 95 (51), 57 (100), and 41 (35). A collected (GLC) sample of the starting dienone **9** was identified with an authentic sample by comparison of ir spectra and GLC retention times. A collected (GLC) sample of the pure ketone **23a** was obtained as a colorless liquid: n^{25}D 1.4488; ir (CCl_4), 1705 (C=O), 1635 (C=C), 1005, and 925 cm^{-1} (CH=CH_2); NMR (CCl_4) δ 5.3–6.2 (1 H, m, vinyl CH), 4.7–5.2 (2 H, m, vinyl CH), 1.8–2.5 (5 H, m, aliphatic CH), 1.09 (9 H, s, *t*-Bu), 0.83 (6 H, s, CH_3), and 0.77 (3 H, d, J = 6 Hz, CH_3); mass spectrum, *m/e* (rel intensity) 210 (M^+, < 1), 168 (12), 153 (12), 85 (19), 69 (43), 57 (100), 55 (26), and 41 (25).

Anal. Calcd for $C_{14}H_{26}O$: C, 79.93; H, 12.46. Found: C, 79,90; H, 12.45.

C. To Dienone 11. The same reaction procedure was repeated with 1.25 mmol of Me_2CuLi and 236 mg (1.0 mmol) of the dienone **11** in 10 ml of Et_2O to yield 237 mg (94%) of the crude ketone **23c** (NMR analyses) which exhibited one major GLC peak (ret time 25.2 min) on a GLC column (Apiezon L on Chromosorb P) where the dienone **11** has a retention time of 14.1 min. A collected (GLC) sample of the pure ketones **23c** was obtained as a colorless liquid: n^{25}D 1.4572; ir (CCl_4) 1705 cm^{-1} (C=O); NMR (CCl_4) δ 5.08 (1 H, t, J = 7 Hz, further partially resolved splitting apparent, vinyl CH), 1.2–2.5 (13 H, m, aliphatic CH including broad singlets at 1.59 and 1.67 attributable to the allylic CH_3 groups), 1.10 (9 H, s, *t*-Bu), 0.84 (6 H, s, CH_3), and 0.73 (3 H, d, J = 7 Hz, CH_3); mass spectrum, *m/e* (rel intensity) 252 (M^+, 1), 195 (32), 128 (83), 123 (65), 95 (28), 83 (25), 69 (100), 57 (73), 55 (20), 43 (54), and 41 (50).

Anal. Calcd for $C_{17}H_{32}O$: C, 80.88; H, 12.78. Found: C, 81.16; H, 12.75.

Reductions with $Cr(en)_2(OAc)_2$. A. The Dienone 10. To a solution of the Cr(II) complex, prepared[10] from 3.94 g (21 mmol) of $[Cr(OAc)_2]_2H_2O$, 2.1 ml (49 mmol) of $H_2NCH_2CH_2NH_2$, 2.1 ml (3.3 mmol) of HOAc, and 40 ml of MeOH, was added a solution of 250 mg (1.2 mmol) of the dienone **10** in 10 ml of MeOH. The resulting solution was stirred at 25° for 14 hr and then diluted with 30 ml of ice water, acidified (HCl) to pH 3, and extracted three times with Et_2O. The Et_2O extract was washed successively with aqueous NaCl, aqueous $NaHCO_3$, and aqueous NaCl and then dried and concentrated. The residual crude product (216 mg) contained (NMR analysis and GLC, Apiezon L on Chromosorb P) the ketone **22b** (ca. 30% corresponding to a 26% yield, ret time 15.2 min) and the dienone **10** (ca. 70% corresponding to a 61% recovery, 13.2 min). Collected (GLC) samples of both materials were identified with previously described authentic samples by comparison of ir spectra and GLC retention times.

B. The Dienone 9. The same reduction procedure was repeated with 21 mmol of the Cr(II) complex and 210 mg (1.08 mmol) of the dienone **9** in 40 ml of MeOH to yield 189 mg of crude product containing (NMR analysis and GLC, Apiezon L on Chromosorb P) the ketone **22a** (ca. 83% corresponding to a 74% yield, ret time 19.2 min) and the dienone **9** (ca. 17% corresponding to 15% recovery, 17.4 min). Collected (GLC) samples of each of the products were identified with authentic samples by comparison of ir spectra and GLC retention times.

C. The Dienone 11. Reduction of 232 mg (0.98 mmol) of the dienone **11** with 21 mmol of the Cr(II) complex in 40 ml of MeOH as previously described yielded 208 mg of crude product containing (NMR analysis and GLC, silicone fluid, SE-30, on Chromosorb P) the ketone **22c** (ca. 53% corresponding to a 48% yield, ret time 15.9 min), and the dienone **11** (ca. 47% corresponding to 42% recovery, 12.0 min). A collected (GLC) sample of the product **22c** was identified with an authentic sample by comparison of ir spectra and GLC retention times. Since attempts to collect the starting dienone **11** from the reaction mixture by GLC resulted in some isomerization (presumably acid catalyzed), further evidence for the identity of the materials in the reaction mixture was obtained by TLC analysis with a silica gel coating. In one solvent system [Et_2O–hexane, 5:95 (v/v)] the R_f values were 0.42 for the starting dienone **11** and 0.48 for the product ketone **22c**; in a second solvent [Et_2O–hexane–acetone, 5:92:3 (v/v/v)] the R_f values were 0.32 for **11** and 0.37 for **22c**.

Reactions of the Cyclopropyl Enone 13. A. Addition of MeLi. To a cold (0°) solution of 314 mg (1.87 mmol) of the enone **13** in 10 ml of Et_2O was added 1.3 ml of an Et_2O solution containing 2.18 mmol of MeLi. After the solution has been stirred at 0° for 40 min, it was washed successively with aqueous NH_4Cl and with aqueous NaCl and then dried and concentrated. The residual crude alcohol **26** (324 mg or 94%, a colorless liquid identified by ir and NMR analysis) was distilled under reduced pressure (1 mm) in a short-path still to separate the pure alcohol **26** as a colorless liquid: n^{25}D 1.4662; ir (CCl_4) 3590 (OH) and 3060 cm^{-1} (cyclopropyl CH); NMR (CCl_4) δ 5.53 (1 H, d, J = 16 Hz, vinyl CH), 5.21 (1 H, d, J = 16 Hz, vinyl CH), 1.5 (7, H, broad, two CH_3 and OH, 1 H exchanged with D_2O), 0.89 (9 H, s, *t*-Bu), and 0.51 (4 H, broad, cyclopropyl CH); mass spectrum, *m/e* (rel intensity), 182 (M^+, 2), 125 (100), 107 (70), 91 (35), 83 (40), 81 (57), 79 (29), 57 (51), 55 (41), 43 (67), 41 (62), and 39 (26).

Anal. Calcd for $C_{12}H_{22}O$: C, 79.06; H, 12.16. Found: C, 79.00; H, 12.18.

B. Reduction with Li and *t*-BuOH in NH_3. To a cold (−78°) solution of 387 mg (55.3 mg-atoms) of Li in 30 ml of NH_3 was added, dropwise and with stirring, a solution of 410 mg (2.5 mmol) of the enone **13** and 222 mg (3.0 mmol) of *t*-BuOH in 5 ml of Et_2O. The resulting solution was stirred under reflux (−33°) for 5 min and then NH_4Cl was added to consume the excess Li and the NH_3 was allowed to evaporate. The residual material was partitioned between Et_2O and aqueous NaCl and the Et_2O layer was concentrated. A solution of the organic residue in 20 ml of cold (0°) acetone was treated with 4 ml of aqueous 8 N H_2CrO_4 and the resulting cold solution was stirred for 10 min and then treated with 5 ml of *i*-PrOH. The reaction mixture was partitioned between Et_2O and aqueous $NaHCO_3$ and the Et_2O layer was washed with aqueous NaCl, dried, and concentrated. The crude liquid product, ketone **27** (317 mg or 75%, ir and nmr analysis), exhibited a single GLC peak (Carbowax 20 M on Chromosorb P) with a retention time of 5.7 min under conditions where the retention time of the starting enone **13** was 15.3 min. A pure sample of the ketone **27** was collected (GLC) as a colorless liquid: n^{25}D 1.4353; ir (CCl_4) 3065 (cyclopropyl CH) and 1708 cm^{-1} (C=O); NMR (CCl_4) δ 2.3–2.7 (2 H, m, CH_2CO), 1.3–1.6 (2 H, m, CH_2), 1.09 (9 H, s, *t*-Bu), 1.01 (3 H, s, CH_3), and 0.23 (4 H, broad singlet, cyclopropyl CH); mass spectrum, *m/e* (rel intensity) 168 (M^+, 19), 111 (26), 85 (30), 83 (20), 69 (39), 57 (100), 55 (56), and 41 (53).

Anal. Calcd for $C_{11}H_{20}O$: C, 78.51; H, 11.98. Found: C, 78.56; H, 12.00.

C. Addition of Me_2CuLi. To a cold (0°) solution of Me_2CuLi, prepared from 390 mg (2.05 mmol) of CuI and 4.04 mmol of MeLi, in 12.4 ml of Et_2O, was added a solution of 300 mg (1.65 mmol) of the enone **13** in 2 ml of Et_2O. The resulting solution was stirred at 0° for 40 min and then washed successively with aqueous NH_4Cl and with aqueous NaCl and dried and concentrated. The residual liquid product (285 mg) contained (NMR and ir analysis) the ketone **28** (estimated yield 75%) accompanied by a minor amount of the alcohol **26**. GLC analysis (Carbowax 20 M on Chromosorb P) indicated the presence of the ketone **28** (ret time 12.4 min, ca. 93%) accompanied by a minor product (5.6 min, ca. 7%) believed to be the olefin [ir (CCl_4) 3060 (cyclopropyl CH), 1630 (C=C), and 890 cm^{-1} (C=CH_2)] obtained by dehydration of alcohol **26**. A pure sample of ketone **28** was collected (GLC) as a colorless liquid: n^{25}D 1.4380; ir (CCl_4), 3060 (cyclopropyl CH) and 1705 cm^{-1} (C=O); NMR (CCl_4) δ 2.43 (2 H, d, J = 6.5 Hz, CH_2CO), 1.2–1.8 (1 H, m, CH), 1.06 (9 H, s, *t*-Bu), 0.8–1.0 (6 H, m, CH_3 including a CH_3 singlet at 0.93), and 0.2–0.4 (4 H, m, cyclopropyl CH); mass spectrum, *m/e* (rel intensity) 182 (M^+, 7), 167 (21), 125 (25), 83 (33), 57 (100), 55 (63), and 41 (32).

Anal. Calcd for $C_{12}H_{22}O$: C, 79.06; H, 12.16. Found: C, 79.12; H, 12.19.

The reaction was repeated by cooling a preformed solution of 1.6 mmol of Me_2CuLi in 12 ml of Et_2O to −40° followed by addition of a solution of 249 mg (1.50 mmol) of the enone **13** in 2 ml of Et_2O. The resulting mixture was stirred at −35 to −45° for 3 hr and then warmed to −12°, quenched by the addition of 2 ml of HOAc in 5 ml of MeOH, and subjected to the usual isolation procedure. The crude product (220 mg or 71%) contained (GLC and NMR analyses) the ketone **28** with no other product being detected. An attempt to effect this same reaction at −78° during a period of 1.5 hr resulted in the recovery of a crude product that contained (GLC and NMR analyses) mainly the starting enone **13** (26.9 min) accompanied by a small amount of the ketone **28** (13.7 min).

Preparation of the Bromide 45. To a cold (0°) solution of 12.69

g (100 mmol) of the aldehyde **43** (contaminated with 6% of a double-bond isomer)[5] in 400 ml of MeOH was added, portionwise and with stirring during 5 min, 10.0 g (260 mmol) of $NaBH_4$. The resulting solution was allowed to warm to 25°, stirred for 12 hr, and then concentrated and partitioned between aqueous NH_4Cl and Et_2O. The ethereal layer was washed with aqueous NaCl, dried, and concentrated to leave a crude liquid containing (GLC, silicone SE-30 on Chromosorb P) the alcohol **44** (ret time 10.1 min) but no starting aldehyde **43** (6.2 min). Distillation separated 9.78 g (76%) of the alcohol **44** as a colorless liquid: bp 97–98° (45 mm); $n^{25}D$ 1.4425; ir (CCl_4), 3630 (OH), 1640 (C=C), and 908 cm^{-1} ($CH=CH_2$); NMR (CCl_4) δ 4.7–6.1 (3 H, m, vinyl CH), 3.23 (3 H, broad singlet, CH_2OH, 1 H exchanged with D_2O), 1.0–2.3 (4 H, m, CH_2), and 0.84 (6 H, s, CH_3); mass spectrum, *m/e* (rel intensity) 128 (M^+, < 1), 110 (11), 97 (52), 95 (22), 81 (32), 55 (100), 43 (44), 41 (60), and 39 (24).

Anal. Calcd for $C_8H_{16}O$: C, 74.94; H, 12.58. Found: C, 74.96; H, 12.58.

Following general procedures described previously,[31] 8.6 g (26 mmol) of CBr_4 was added, portionwise and with stirring during 10 min, to a solution of 3.2 g (25 mmol) of the alcohol **44** and 7.7 g (29 mmol) of Ph_3P in 20 ml of CH_2Cl_2. After the addition, accompanied by an exothermic reaction, was complete, the resulting pale yellow solution was stirred at 25° for 5.5 hr and then distilled under reduced pressure. The product was collected as 7.52 g fractions (bp 30–72° (25–60 mm); $n^{25}D$ 1.5037–1.5080) that contained (GLC, Carbowax 20 *M* on Chromosorb P) ca. 4% of a bromo olefin (ret time 15.0 min) isomeric with **45**, 55–63% of the bromo olefin **45** (17.7 min), and 33–41% of $CHBr_3$ (34.2 min, a collected sample was identified from its mass spectrum). A collected (GLC) sample of the pure bromo olefin **45** was obtained as a colorless liquid: $n^{25}D$ 1.4662; ir (CCl_4), 1740 (C=C), and 905 cm^{-1} ($CH=CH_2$); NMR (CCl_4) δ 4.7–6.2 (3 H, m, vinyl CH), 3.23 (2 H, s, CH_2Br), 1.2–2.3 (4 H, m, CH_2), and 1.00 (6 H, s, CH_3); mass spectrum, *m/e* (rel intensity) 192 (M^+, 1), 190 (M^+, 1), 137 (22), 135 (22), 111 (72), 97 (40), 70 (25), 69 (100), 55 (62), 54 (55), 43 (25), 41 (69), and 39 (27).

Anal. Calcd for $C_8H_{15}Br$: C, 50.25; H, 7.91; Br, 41.84. Found: C, 50.25; H, 7.92; Br, 41.73.

Authentic samples of the cyclopentane **46** and the cyclohexane **48** were obtained from Chemical Samples Co. A previously described[32] modification of the Wolff–Kishner reduction was followed with 4.5 g (36 mmol) of the aldehyde **43**, 10 ml of hydrazine hydrate, 12 ml of ethylene glycol, and 10 g of KOH. The neutral volatile products that distilled included some unchanged aldehyde **43**, the olefin **47**, and other unidentified materials. A collected (GLC, Carbowax 20 *M* on Chromosorb P) sample of the olefin **47** was obtained as a colorless liquid: $n^{25}D$ 1.4015 (lit.[33] bp 99–101°, $n^{25}D$ 1.4012); ir (CCl_4) 1640 C=C) and 905 cm^{-1} ($CH=CH_2$); NMR (CCl_4) δ 4.8–6.2 (3 H, m, vinyl CH), 1.1–2.3 (4 H, m, CH_2), and 0.93 (9 H, s, *t*-Bu); mass spectrum, *m/e* (rel intensity) 112 (M^+, 7) 97 (35), 57 (100), 56 (36), 55 (78), 43 (44), 41 (48), and 39 (37).

Reaction of the Bromide 45 with *n*-Bu_3SnH. A solution of 316 mg (1.65 mmol) of the bromide **45** and 5 mg of $(CH_3)_2C(CN)N=NC(CN)(CH_3)_2$ (AIBN) in 3.0 ml of benzene was purged with purified N_2 to remove dissolved O_2 and then 380 mg (1.35 mmol) of *n*-Bu_3SnH was added. The resulting reaction vessel was sealed and heated to 69° for 6 hr. The resulting reaction solution contained (GLC, Carbowax 20 *M* on Chromosorb P) several unidentified minor, low-boiling components (ret times 5.3, 6.0, 7.7 min), the cyclopentane **46** (16.6 min), the olefin **47** (20.3 min), and PhH (43 min). On a second GLC column (TCEP on Chromosorb P) where the retention times of the cyclopentane **46** and the olefin **47** (not resolved) were 5.0 min, the absence of the cyclohexane **48** (6.4 min) was demonstrated. At higher temperature with this same GLC column (TCEP) where the retention time of the cyclopentane **46** was 4.0 min, the unchanged bromide **45** (31.4 min) was also found. The best resolution of the cyclopentane **46** and the olefin **47** was obtained on a glpc column (15% $AgNO_3$ in Carbowax on Chromosorb P) where the retentions were: **46**, 12.2 min; and **47**, 15.4 min. Using this latter column (calibrated with known mixtures) the composition of the hydrocarbon product was 86% of **46** and 14% of **47**.

A collected (GLC) sample of the bromide **45** was identified by comparison of GLC retention times and ir spectra and collected samples of the cyclopentane **46** and the olefin **47** were identified with an authentic samples by comparison of GLC retention times and ir and mass spectra. A sample of the PhH peak was also collected (GLC) and its mass spectrum determined to demonstrate the absence of higher molecular weight components that were unresolved from this GLC peak. Another GLC column [neopentyl glycol adipate (NGA) on Chromosorb P] also exhibited only major peaks corresponding to the cyclopentane **46** and the olefin **47** (unresolved, 15.8 min) and PhH (36.1 min) and lacked a peak corresponding to the cyclohexane **48** (32.3 min). The reaction was repeated with 135 mg (0.71 mmol) of bromide **45**, 171 mg (0.61 mmol) of *n*-Bu_3SnH, and 5 mg of AIBN in 1.2 ml of PhH. After the reaction was complete, 53 mg of $PhCH_3$ was added as an internal standard for GLC analysis. The composition of the hydrocarbon product was 89% of **46** and 11% of **47** and the calculated yields (based on the starting bromide **45** and employing GLC equipment calibrated with known mixtures) were 62% yield of the cyclopentane **46**, 8% yield of the olefin **47**, and 27% recovery of the bromide **45**.

References and Notes

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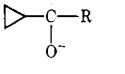
(2) (a) H. O. House and P. D. Weeks, *J. Am. Chem. Soc.*, Part VI in this issue (b) *ibid.*, Part VIII in this issue.
(3) C. Walling and A. Cioffari, *J. Am. Chem. Soc.*, **94**, 6059 (1972).
(4) K. U. Ingold in "Free Radicals", Vol. 1, J. K. Kochi, Ed., Wiley-Interscience, New York, N.Y., 1973, pp 37–112; D. Lal, D. Griller, S. Husband, and K. U. Ingold, *J. Am. Chem. Soc.*, **96**, 6355 (1974).
(5) H. O. House, W. C. Liang, and P. D. Weeks, *J. Org. Chem.*, **39**, 3102 (1974).
(6) H. O. House, D. S. Crumrine, A. Y. Teranishi, and H. D. Olmstead, *J. Am. Chem. Soc.*, **95**, 3310 (1973).
(7) (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).
(8) We have recently repeated these measurements on a solution of anion radical **19** in DMF and obtained the same kinetic values reported previously.[7a]
(9) It is of interest to note that this rate difference corresponds to an increase in activation energy of ca. 8 kcal/mol or more which is a substantial fraction of the estimated resonance energy, 10–13 kcal/mol, for an allyl radical: D. M. Golden, N. A. Gac, and S. W. Benson, *J. Am. Chem. Soc.*, **91**, 2136 (1969); W. von E. Doering and G. H. Beasley, *Tetrahedron*, **29**, 2231 (1973).
(10) H. O. House and E. F. Kinloch, *J. Org. Chem.*, **39**, 1173 (1974).
(11) H. O. House and M. J. Umen, *J. Am. Chem. Soc.*, **94**, 5495 (1972); *J. Org. Chem.*, **38**, 3893 (1973).
(12) (a) R. B. Bates, G. Büchi, T. Matsuura, and R. R. Shaffer, *J. Am. Chem. Soc.*, **82**, 2327 (1960); (b) R. E. Corbett and R. N. Speden, *J. Chem. Soc.*, 3710 (1958); (c) D. S. Caine and J. T. Gupton, to be published; (d) for a recent survey, see D. S. Caine, *Org. React.*, in press.
(13) (a) J. A. Marshall and R. A. Ruden, *J. Org. Chem.*, **37**, 659 (1972); (b) G. Daviaud and Ph. Miginiac, *Tetrahedron Lett.*, 997 (1972); (c) W. G. Dauben and W. M. Welch, *ibid.*, 4531 (1971); (d) E. J. Corey and P. L. Fuchs, *J. Am. Chem. Soc.*, **94**, 4014 (1972); (e) P. A. Grieco and R. Finkelhor, *J. Org. Chem.*, **38**, 2100 (1973).
(14) H. O. House, L. E. Huber, and M. J. Umen, *J. Am. Chem. Soc.*, **94**, 8471 (1972). We presume that the reduction potential for the alkylidene malonate **38** will be less negative than the value, −2.13 V vs. SCE, determined for $(CH_3)_2C=C(CO_2Et)_2$.
(15) E. D. Bergmann, D. Ginsberg, and R. Pappo, *Org. React.*, **10**, 205 (1959).
(16) We are indebted to Professor D. S. Caine and J. T. Gupton for samples of the enones **30** and **31**. The preparation of enone **30** was described in ref 12a and by D. Caine and P. F. Ingwalson, *J. Org. Chem.*, **37**, 3751 (1972). The enone **31** has been described by A. E. Greene, J.-C. Muller, and G. Ourisson, *Tetrahedron Lett.*, 4147 (1971).
(17) In contrast to the behavior of cyclopropyl enones, simple cyclopropyl ketones are reduced by metals in NH_3 with ring opening: S. W. Staley, *Sel. Org. Transform.*, **2**, 309 (1972). This ring opening reaction with simple cyclopropyl ketones presumably reflects the more rapid rearrangement, analogous to 7 → 8, with localized radical ions of the type



(18) (a) C. Walling and A. Cioffari, *J. Am. Chem. Soc.*, **94**, 6059, 6064 (1972); (b) A. L. J. Beckwith, I. A. Blair, and G. Phillipou, *Tetrahedron Lett.*, 2251 (1974); for related studies, see A. L. J. Beckwith, I. Blair, and G. Phillipou, *J. Am. Chem. Soc.*, **96**, 1613 (1974); A. L. J. Beckwith and G. Moad, *Chem. Commun.*, 472 (1974); (c) for a recent review of radical cyclization reactions, see M. Julia, *Acc. Chem. Res.*, **4**, 386 (1971); (d) E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, "Confor-

mational Analysis", Wiley-Interscience, New York, N.Y., 1966, p 191.
(19) 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 proton NMR spectra were determined at 60 mHz with a Varian, Model A-60 or Model T-60, NMR 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 intermedlates were performed under a nitrogen atmosphere.
(20) Z. Majerski and P. v. R. Schleyer, *J. Org. Chem.*, **34**, 3215 (1969).
(21) R. S. Shank and H. Shechter, *J. Org. Chem.*, **24**, 1825 (1959).
(22) E. F.Cox, M. C. Caserio, M. S. Silver, and J. D. Roberts, *J. Am. Chem. Soc.*, **83**, 2719 (1961).
(23) J. C. Collins and W. W. Hess, *Org. Syn.*, **52**, 5 (1972).
(24) R. Ratcliffe and R. Rodehorst, *J. Org. Chem.*, **35**, 4000 (1970).
(25) The gummy Cr-salt residue was easily removed from the glassware by washing with aqueous NaOH, KOH, or Na_2CO_3.
(26) D. I. Schuster and J. D. Roberts, *J. Org. Chem.*, **27**, 51 (1962).
(27) H. O. House, D. Koepsell, and W. Jaeger, *J. Org. Chem.*, **38**, 1167 (1973).
(28) N. N. Gaidamovich and I. V.Torgev, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1803 (1961).
(29) We are indebted to Professor J. A. Marshall for providing us with the Ir spectrum of an authentic sample.
(30) G. B. Kauffman and L. A. Teter, *Inorg. Syn.*, **7**, 9 (1963).
(31) (a) R. G. Weiss and E. I. Snyder, *J. Org. Chem.*, **36**, 403 (1971); (b) J. Hooz and S. S. H. Gilani, *Can. J. Chem.*, **46**, 86 (1968); (c) I. M. Downie, J. B. Holmes, and J. B. Lee, *Chem. Ind. (London)*, 900 (1966).
(32) E. Renk, P. R. Shafer, W. H. Graham, R. H. Mazur, and J. D. Roberts, *J. Am. Chem. Soc.*, **83**, 1987 (1961).
(33) J. W. H. Faber, J. Van den Berghe, and K. R. Dunham, French Patent 1,423,429, Jan. 3, 1966; *Chem. Abstr.*, **66**, 29360 (1967).

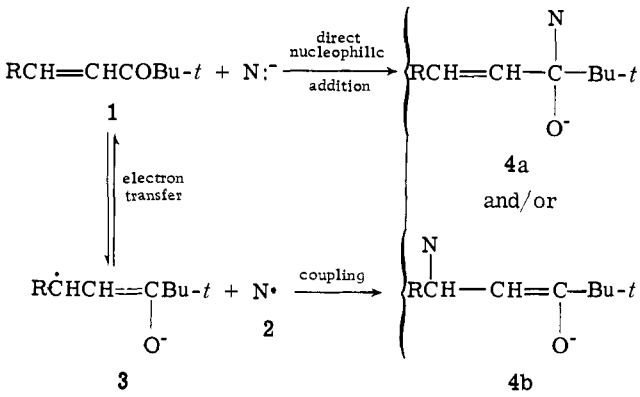
Reactions Involving Electron Transfer. VIII. The Reaction of Tritylllithium with Enones[1]

Herbert O. House* and Paul D. Weeks

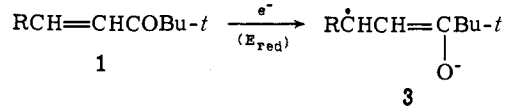
Contribution from the School of Chemistry, Georgia Institute of Technology, Atlanta, Georgia 30332. *Received November 1, 1974*

Abstract: The reaction of a DME solution of Ph_3CLi with several unsaturated ketones **9–13** has been studied. With the easily reduced enone **9**, a product of the general structure **19** was formed rapidly while with the difficultly reduced ketone **10**, a product of the general structure **18** was formed slowly. With the enones **11** and **12** having intermediate reduction potentials, the product structure **18** or **19** appeared to be determined by the steric environment at the β carbon. The difficultly reduced cis enone **13** reacted rapidly with Ph_3CLi to form a stable vinyl enolate anion **28** that reacted with D_2O to form a mixture of this cis enone **30** and the trans enone **29**.

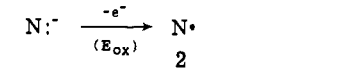
In two accompanying papers[2] we have considered some of the possible consequences of a change in mechanism from the direct addition of a nucleophile, $N:^-$, to an enone **1** to a two-step process proceeding by way of the ion radical intermediates **2** and **3**. The possibility that a given reaction



could proceed by the initial transfer of only an electron from $N:^-$ to the enone **1** can be estimated from consideration of the electrode potential, E_{red}, of the enone **1** (eq 1) and the electrode potential, E_{ox}, of the nucleophile (eq 2). If the value of E_{ox} (eq 2) equals or is more negative than E_{red} (eq 1, typical values -1.4 to -2.5 V vs. SCE),[3] the initial electron transfer from $N:^-$ to the enone **1** is energetically favorable. As the reduction potential of the enone **1** (E_{red}) becomes more negative than the electrode potential for the nucleophile (E_{ox}), the transfer of an electron rapidly becomes unfavorable. For example, if the two redox reactions (eq 1 and 2) are reversible and E_{red} is 0.3 V more negative than E_{ox}, a solution containing 1 *M* enone **1** and 1 *M* nucleophile $N:^-$ would produce the radical intermediates **2** and **3** in concentrations no higher than 10^{-3} *M*. If the potential difference $E_{red} - E_{ox}$ becomes more negative than -0.4 V, the concentrations of **2** and **3** will become so low (10^{-4} or less) that the rate of the bimolecular reaction **2** + **3** → **4** will become insignificant.[4]



(1)



(2)

Consequently, in any example where the potential values E_{red} and E_{ox} are known, one can predict that a reaction of the type **1** + $N:^-$ → **2** + **3** → **4** is energetically reasonable only in cases where the potential difference $E_{red} - E_{ox}$ is less negative than -0.4 V. However, it must be noted that this prediction is only reliable for reactions where the initial transfer of an electron is not accompanied by transfer of an associated atom.[5]

At least part of the data needed for the foregoing prediction is available since the reduction potentials (E_{red}) for most enones and related unsaturated carbonyl compounds can be estimated with reasonable accuracy.[3] Normally, the reduction potentials for these compounds, determined in