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(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 intermediates were performed under a nitrogen atmosphere.
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Reactions Involving Electron Transfer. VIII. The Reaction of Trityllithium with Enones[1]

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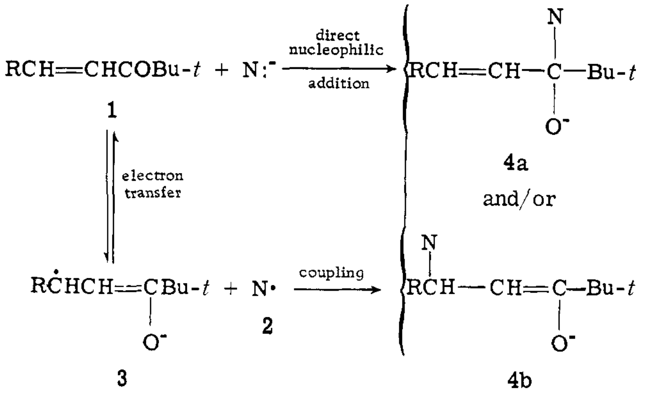
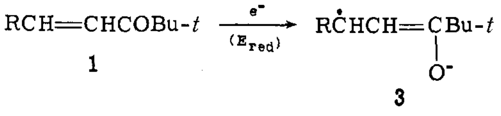
Abstract: The reaction of a DME solution of Ph_3CLi with several unsaturated ketones **9–13** has been studied. With the easily reduced enone **9**, a product of the general structure **19** was formed rapidly while with the difficultly reduced ketone **10**, a product of the general structure **18** 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]





$$\mathrm{RCH{=}CHCOBu\text{-}}t \xrightarrow[(E_{red})]{e^-} \mathrm{R\dot{C}HCH{=}\underset{\underset{\displaystyle O^-}{|}}{C}Bu\text{-}}t \qquad (1)$$

1 3

$$\underset{}{\mathrm{N}:^-} \xrightarrow[(E_{ox})]{-e^-} \underset{2}{\mathrm{N}\cdot} \qquad (2)$$

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

Table I. Electrode Potential Values Obtained by Cyclic Voltammetry for the Oxidation of Some Representative Carbanionic Intermediates

Compd (concn, *M*)	Solvent	Supporting electrolyte (concn, *M*)	$E_{1/2}$, V vs. SCE	Estimated half-life of radical, sec
Ph_3CLi (0.034) (**5**)	DME	$LiClO_4$ (0.17)	−1.3[a]	~5
Ph_2CHLi (0.03–0.06) (**6**)	DME	$LiClO_4$ (0.15–0.17)	−1.1	<1[b]
$Ph(H)C{=}C(O^-Na^+)CH_3$ (0.09–0.15) (**7**)[c]	DMF	n-Bu_4NBF_4 (0.5)	−0.2	<0.1[b]
$(EtO_2C)_2CH^-Na^+$ (0.034–0.055) (**8**)	DMF	n-Bu_4NBF_4 (0.5)	+0.4	<0.1[b]

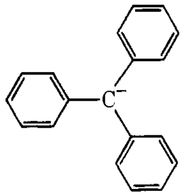
[a] A second oxidative current peak was observed at ca. +0.4 V vs. SCE. The reported values (ref 6) vs. an Ag|AgCl (sat) reference electrode are −1.335 V and +0.31 V, corresponding to −1.38 V vs. SCE and +0.27 V vs. SCE. [b] No reduction peak was observed during the reverse scan. [c] The stereoisomer with the Ph and CH_3 groups trans.

aprotic solvents, lie within the range −1.4 V to −2.5 V (vs. SCE).

Electrode potential data derived from the electrochemical oxidation of carbon nucleophiles (e.g., eq 2) are much less readily available; to our knowledge the only available values related to a standard reference electrode are those derived from a study of the electrochemical oxidation of the trityl anion, the cyclopentadienyl anion, and several derivatives of the cyclopentadienyl anion.[6] In order to gain a better idea of the electrode potentials involved in the oxidation of various typical carbanionic intermediates, we have examined the electrochemical oxidation of DME solutions of Ph_3CLi (**5**) and Ph_2CHLi (**6**) as well as the corresponding oxidations of DMF solutions of the enolate anions **7** and **8.**[7] Among these four compounds (see Table I), only the oxidation of Ph_3CLi formed a radical of sufficient stability to be detected during the reverse cyclic voltammetry scan. The $E_{1/2}$ value obtained for Ph_3CLi which corresponded reasonably well to the value previously reported,[6] was the most negative of the four values measured and was more than 1.0 V more negative than either of the enolate anions **7** or **8.** Consideration of these and related[6] data suggests that the stabilized carbanions with the most negative electrode potentials (i.e., the best reducing agents) are those anions which can be oxidized to form relatively stable free radicals (e.g., $Ph_3C\cdot$ from Ph_3C^-). In keeping with this idea, a study of the electrochemical oxidation of the malonate anion **8**[8] indicated the formation of a rather reactive radical, $(EtO_2C)_2CH\cdot$, that rapidly abstracted a hydrogen atom from the solvent (EtOH, HMP, *N,N*-dimethylacetamide). Thus far, our efforts to obtain $E_{1/2}$ values for the reactive, covalent organometallic compounds CH_3Li and $(CH_3)_2CuLi$ have been thwarted by the fact that both of these compounds are rapidly decomposed upon addition to a DME solution of $LiClO_4$ or n-Bu_4NBF_4.

The foregoing data indicate that reactions of the type **1** + $N:^- \rightarrow$ **2** + **3** $\rightarrow$ **4** are not likely to be observed when the nucleophile, $N:^-$, is an alkali metal enolate anion because the electrode potential, E_{ox}, will be more than 1.0 V less negative than the value of E_{red} for a typical enone. In fact, nucleophiles with sufficiently negative electrode potentials to transfer an electron to a typical enone[9] would appear to be limited to rather special stabilized carbanions such as **5** and **6** and to various organic derivatives of transition metals that have electrode potentials more negative than −1.0 V vs. SCE.[10]

Since the electrode potential of Ph_3CLi in DME solution was sufficiently negative (ca. −1.3 V vs. SCE) that it should be capable of reducing certain unsaturated carbonyl, we undertook an investigation of the reaction of a DME solution of Ph_3CLi with a group of unsaturated carbonyl compounds **9–14.** This group of carbonyl compounds has a range of reduction potentials (given below the structures **9–14** as volts vs. SCE) from −1.4 to −2.2 V. Since Ph_3CLi reacts rapidly with enolizable ketones to form enolate anions,[11] each of the α,β-unsaturated ketones **9–14** selected contained no hydrogen at either the λ carbon or the α′ carbon. Our selection of Ph_3CLi as a nucleophile was prompted both by the relatively negative electrode potential (−1.3 V vs. SCE) of the compound and by earlier publications suggesting that electron distribution in the π system of the anion **15** and the radical **16** may differ.



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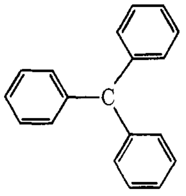
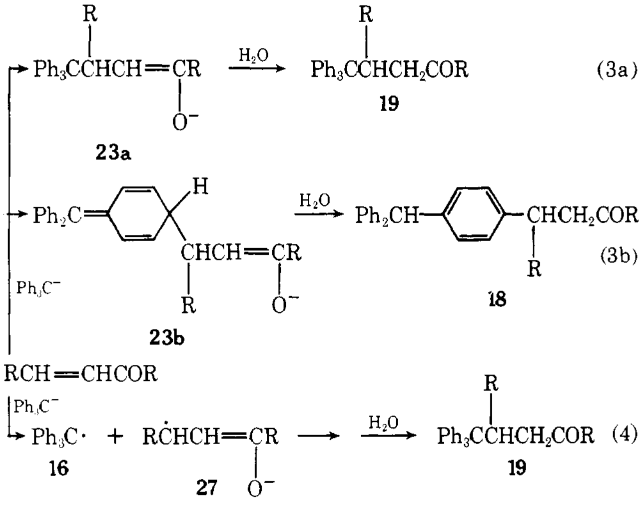


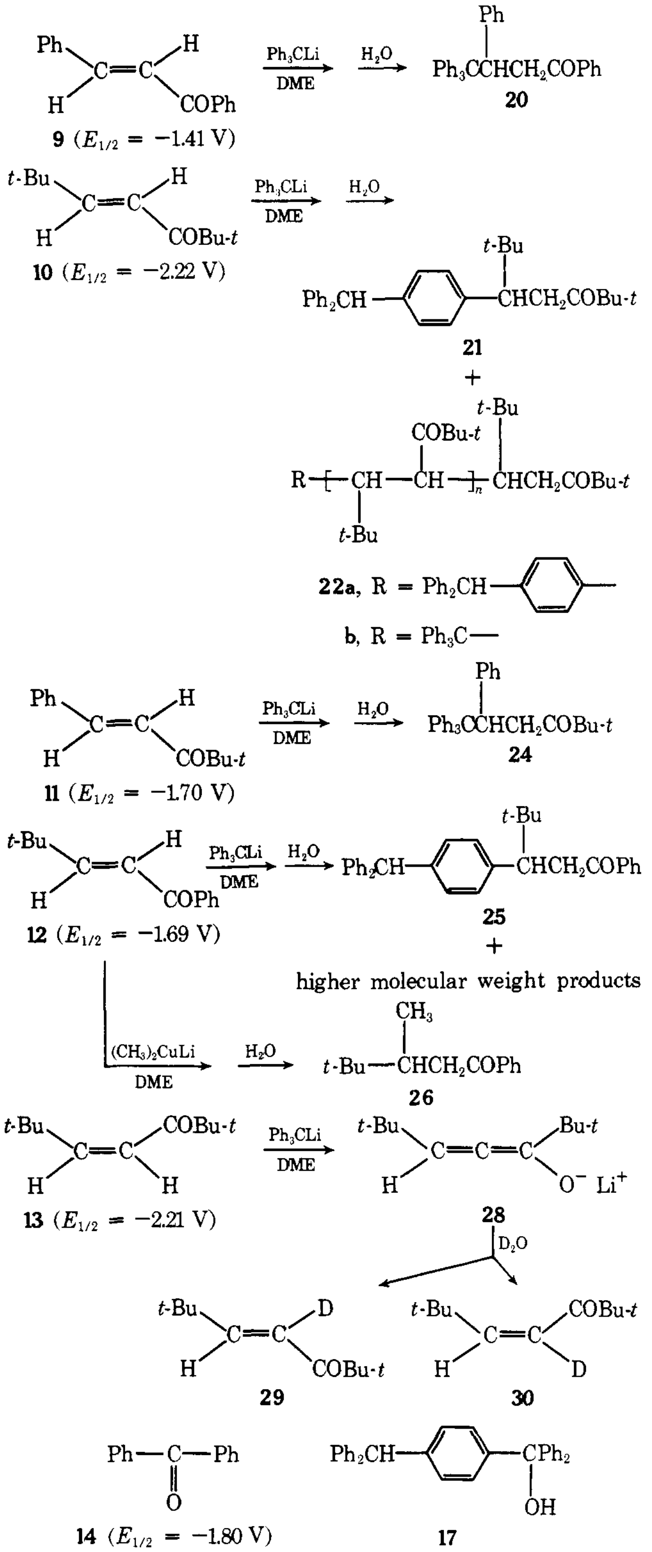
16

NMR studies of Ph_3CLi[7b-d] as well as the crystal structure of a derivative[12] indicate that a substantial fraction of the negative change in this carbanion is distributed in the phenyl rings. The estimated distribution,[7b,d] 13% at each para position and 8% at each meta position, would suggest that in the anion **15,** the electron densities at the central carbon atom and at each para position are similar. Consequently, one might expect reactions of the anion **15** with nucleophiles to occur both at the central carbon and at the para position of one of the phenyl rings. Some indication that this expectation is correct is derived from the fact that Ph_3CLi reacts with CO_2 to form triphenylacetic acid (attack at the central carbon) but this reagent in tetrahydropyran solution reacts with benzophenone (**14**) to yield the alcohol **17** (attack at a para position).[13a,b]

Epr studies of the trityl radical **16,** including study of the radical **16** with excess ^{13}C at the central carbon atom,[14] suggest that about 65% of the spin density in the radical resides at the central carbon atom. Thus, one might anticipate that, in the absence of serious steric interference, coupling of the trityl radical **16** with a second radical should show a preference for attack at the central carbon atom. Consideration of the foregoing data suggested that although reactions involving direct nucleophilic addition of Ph_3C^- (eq 3) could be expected to form products of either general structure **18** or **19,** reactions proceeding by initial electron transfer (eq 4) should favor products of the general structure **19.**



Scheme I



To explore this idea, solutions of Ph_3CLi in DME were initially allowed to react with the ketones **9** and **10.** In the reaction with ketone **9,** where $E_{red} - E_{ox} \sim -0.1$ V so that initial electron transfer is energetically reasonable, the red color of the Ph_3C^- anion was discharged rapidly when the Ph_3CLi solution was added to the enone **9** until approximately 0.75 equiv of Ph_3CLi had been added. After the addition of excess Ph_3CLi and reaction for 10 min at 25°, H_2O was added and the product **20** was isolated in 80% yield. That the product had structure **20** (analogous to **19**), and not a structure of the type **18,** was apparent both from the absence of NMR absorption in the region δ 5.5 (characteristic of Ar_3CH) and from the presence of an abundant fragment ion at *m/e* 243 (Ph_3C^+) in the mass spectrum of **20.**

By contrast, when a solution of Ph_3CLi was added to the enone **10,** where $E_{red} - E_{ox} \sim -0.9$ V and initial electron transfer is very unlikely, the red color of the Ph_3C^- anion was not discharged even in the early stages of the addition and the bulk of the unchanged enone **10** was recovered when the reaction mixture was quenched with H_2O after 10 min at 25°. Even after a reaction period of 3 hr followed by quenching with D_2O, 19% of the unchanged (and nondeuterated) enone **10** was recovered. After reaction for 3–4 hr at 25°, the principal products were the ketone **21** (23% yield) and a mixture of higher molecular weight materials believed to be one of the structures **22** formed by the relatively slow Michael addition of an intermediate such as **23** to the unchanged enone **10.**[15] Neither the cis enone **13** or the dihydro dimers[16] derived from enones **10** and **13** were detected (GLC) among the reaction products. In keeping with the assignment of structure **21** to the monomeric product, the material exhibited an NMR singlet at δ 5.52 and exhibited only a very low intensity fragment peak at *m/e* 243 in its mass spectrum. In an analogous experiment, in which the reaction solution was quenched with D_2O, the isolated ketone **21** was found to contain a mixture of d_1, d_2, and d_3 species as might be expected if an intermediate such as **23b** had been formed initially.

We then examined reactions with several ketones **11, 12,** and **14** where the values $E_{red} - E_{ox}$ were in the range −0.4 to −0.5 V. In DME solution we observed no evidence for reaction of Ph_3CLi with PhCOPh (**14,** $E_{red} - E_{ox} = -0.5$ V); after 4 hr at 25° when the solution was hydrolyzed we recovered only Ph_3CH and the unchanged PhCOPh (**14**). Consequently, use of the tetrahydropyran (expected[7] to be less effective than DME in solvating Li^+) as a solvent is evidently an important feature in the previously described[13b] formation of alcohol **17** from Ph_3CLi and PhCOPh (**14**). The reaction of the enone **11** ($E_{red} - E_{ox} = -0.4$ V) with Ph_3CLi was very similar to reaction with the enone **9.** After a reaction period of 5 min at 25°, the adduct **24** (analogous to **19**) was isolated in 95% yield. We then examined the reaction with the enone **12** ($E_{red} - E_{ox} = -0.4$ V), a compound having essentially the same reduction potential as enone **11** but with a sterically larger substituent (*t*-Bu rather than Ph) at the β carbon. The red color of the Ph_3C^- anion persisted after approximately 0.5 equiv of Ph_3CLi had been added to a solution of the enone **12;** after a reaction period of 15 min at 25°, the mixture was hydrolyzed to give a mixture of Ph_3CH, the starting enone **12** (22% recovery), the ketone **25** (23% yield), and a mixture of higher molecular weight products believed analogous to structures **22.** Thus, although enone **12** reacts with Ph_3CLi much more rapidly than the enone **10,** the product structures are similar. To establish that the enone **12** was capable of undergoing conjugate addition with a reagent thought[2] to react by initial electron transfer, the enone **12** was treated with Me_2CuLi to form the normal adduct **26** in 89% yield. These data suggest that enones **11** and **12** represent borderline cases in which the value $E_{red} - E_{ox}$ (−0.4 V) can allow the formation of low concentrations of intermediates such as **16** and **27.** However, subsequent coupling of these reagents may be retarded sufficiently by steric hindrance so that the rate of competitive direct nucleophilic addition is the more rapid process.

In an effort to study an example of addition to an enone analogous to **10** but with less steric hindrance to β addition, we examined the reaction of the cis enone **13** with Ph_3CLi. Surprisingly, this cis enone **13**[17] reacted rapidly to discharge the red color of 1.0 equiv of Ph_3CLi. However, after hydrolysis with H_2O no adduct was detected; instead, a mixture of the cis enone **13** (17% of the enone product) and the trans enone **10** (83% of the enone product) was formed. This observation suggested that Ph_3CLi reacted as a base with the enone **13** to form the vinyl enolate anion **28**. Verification of this idea was readily obtained by quenching the reaction mixture with D_2O to form a mixture of the monodeuterated enones **29** and **30**.

Although a number of examples are known of the base-catalyzed exchange of an α hydrogen for deuterium in α,β-unsaturated ketones,[18] in many of the earlier cases it is possible that exchange occurred by conjugate addition of ROD and subsequent elimination of ROH. Some recent examples of analogous H-D exchanges with retention of configuration are suggested to involve vinyl enolate anions rather than an addition-elimination sequence.[19] The iron tricarbonyl complex with a dienone also was found to undergo an H-D exchange.[20] More recently, examples of stable vinyl enolate anions have been obtained from certain conjugate additions to α,β-acetylenic esters,[21] and from the reaction of α-bromocinnamic acid with n-BuLi.[22] The presently described reaction of enone **13** with Ph_3CLi to form **28** represents the first example of which we are aware in which the α proton of an α,β-unsaturated ketone has been removed by direct reaction with a strong base to form a stable vinyl enolate anion. Although this proton abstraction is of interest, the fact that it occurs rapidly precludes study of the addition of Ph_3CLi to the enone **13**.

Experimental Section[23]

Preparation of Starting Materials. The preparation and/or characterization of the enones **9, 10, 11, 12,** and **13** has been described in previous publications.[3,16] All anhydrous ethereal solvents were distilled from $LiAlH_4$ immediately before use and commercial halide-free ethereal solutions of MeLi were standardized as previously described.[24] Solutions of Ph_3CLi in DME were obtained by removing the solvent from known amounts of ethereal MeLi under reduced pressure,[24] redissolving the MeLi in anhydrous DME, and adding either an equivalent amount or an excess of Ph_3CH. Since the concentrations of stock solutions of Ph_3CLi in DME slowly diminished with time,[25] the actual Ph_3CLi concentration was determined immediately before use by titration with a standard solution of *sec*-BuOH in xylene[24] until the red color of the Ph_3C^- anion was just discharged.

Reaction of Ph_3CLi with the Trans Enone 10. To a solution of 500 mg (2.98 mmol) of the enone **10** in 10 ml of DME was added, dropwise with stirring during 5 min, 27 ml of a DME solution containing 6.08 mmol of Ph_3CLi (excess Ph_3CH was also present). Even in the early stages of this addition there was no indication that the red color of the Ph_3C^- anion was being discharged.[26] The resulting red solution was stirred at 25° for 4 hr and then partitioned between Et_2O and aqueous NH_4Cl. The ethereal layer was washed with aqueous NaCl, dried, and concentrated. The residue was subjected to preparative TLC on silica gel (E. Merck, No. GF 254) employing an Et_2O-hexane mixture (1:20 v/v) as the eluent. The most rapidly eluted component (R_f 0.86), identified as Ph_3CH by comparison of R_f values and ir spectra, amounted to 1.12 g (66% recovery based on the total amount of Ph_3CLi + Ph_3CH present). The next component (R_f 0.55-0.65) contained (NMR analysis) 283 mg (23%) of the crude solid ketone **21**. The final TLC band eluted (R_f 0.25-0.4) was 532 mg of a mixture of semisolid materials believed to contain a mixture of small polymers having the general structure of **22a** and/or **22b**. A 188-mg portion of the crude ketone **21** was recrystallized twice from Et_2O to separate 130 mg of the ketone **21** as colorless needles, mp 148-149° Subsequent recrystallization from hexane separated the pure ketone **21** as colorless needles: mp 148.5-150.5°; ir (CCl_4) 1710 cm^{-1} (C=O); uv maximum (hexane) 224 mμ (ϵ 19,400) with a series of weak maxima (ϵ 890 or less) in the region 255-273 mμ; NMR ($CDCl_3$) δ 6.8-7.5 (14 H, m, aryl CH), 5.52 (1 H, s, trityl CH), 2.5-3.7 (3 H, m, benzylic CH and CH_2CO), 0.98 (9 H, s, *t*-Bu), and 0.87 (9 H, s, *t*-Bu); mass spectrum, *m/e* (rel intensity) 412 (M^+, 34), 357 (16), 356 (51), 256 (18), 243 (3), 207 (22), 167 (55), 141 (22), 108 (24), 107 (20), 85 (38), 79 (27), 77 (21), 57 (100), and 41 (26). Anal. Calcd for $C_{30}H_{36}O$: M^+, 412.2766. Found: M^+, 412.2789.

Anal. Calcd for $C_{30}H_{36}O$: C, 87.33; H, 8.80. Found: C, 87.08; H, 8.66.

The crude mixture that was eluted last in the chromatographic separation exhibited ir absorption (CCl_4) at 1708 cm^{-1} (nonconjugated C=O) with NMR absorption ($CDCl_3$) qualitatively similar to the NMR absorption of ketone **21**. However, the absorption attributable to aryl and trityl CH groups (δ 6.7-7.6 and 5.3-5.5) was substantially less intense than aliphatic CH absorption in the region δ 2.6-3.4 and 0.8-1.2 suggesting the presence of several aliphatic ketone residues for each trityl group.

In another experiment a solution of 327 mg (1.52 mmol) of the enone **10** in 19 ml of DME was added to 3 ml of a DME solution containing 0.75 mmol of Ph_3CLi. After the red solution had been stirred at 25° for 30 min, the reaction solution was quenched by the addition of 3 ml of D_2O and the crude product was separated as previously described. GLC analysis (silicone SE-52 on Chromosorb P, temperature varied from 90 to 280° at 4°/min) indicated the presence of the trans enone **10** (ret time 7.8 min) and Ph_3CH (42.4 min) and lacked GLC peaks corresponding to the cis enone **13** (9.0 min) and the dihydro dimers derived[16] from enones **10** and **13** (37.2 min). The ketone **21** and higher molecular weight materials were not eluted from this column. The NMR spectrum of a collected (GLC) sample of the enone **10** from this reaction corresponded in all respects to the NMR spectrum of an authentic sample *indicating no substantial incorporation of deuterium into the* enone **10** recovered from the reaction. The experiment was repeated with a solution of 300 mg (1.79 mmol) of the enone **10** and 1.79 mmol of Ph_3CLi in 11 ml of DME that was stirred at 25° for 3 hr and then quenched with D_2O. After the crude product had been mixed with a known weight of n-$C_{12}H_{26}$, analysis (GLC, silicone SE-52 on Chromosorb P, temperature varied from 90 to 290° at 4°/min, apparatus calibrated with a known mixture of authentic samples) indicated the presence of the trans enone **10** (ret time 9.8 min, 19% recovery), n-$C_{12}H_{26}$ (13.7 min), and Ph_3CH (47.0 min). A collected (GLC) sample of the enone **10** was subjected to mass spectrometric analysis and found to contain nondeuterated material with less than 2% d_1 species. From a comparable experiment in which a solution of 2.55 mmol of Ph_3CLi and 372 mg (2.21 mmol) of the enone **10** in 35 ml of DME was stirred for 30 min at 25° and then quenched with D_2O, GLC analysis of the crude product (n-$C_{12}H_{26}$ added) indicated a 6% recovery of the enone **10**. The remaining crude product was subjected to preparative TLC separation and appropriate fractions were recrystallized from Et_2O to separate 65 mg (10% yield) of the ketone **21** (mp 141-143°). Mass spectrometric analysis of this product indicated the presence of 20% d_0, 46% d_1, 29% d_2, and 5% d_3 species. The NMR spectrum of this sample indicated that the bulk of the deuterium is located at the carbon α to the carbonyl group. The remaining fractions separated by this TLC system were eluted and their NMR spectra were examined to determine the ratio of aryl protons (δ 6.8-7.5) to *t*-Bu protons (δ 0.8-1.1). Since only the fraction containing ketone **21** exhibited a ratio (ca. 14 aryl H's/18 *t*-Bu H's) corresponding to a 1:1 adduct from the enone **10** and Ph_3CLi, we believe that no other 1:1 adduct was present in substantial amount.

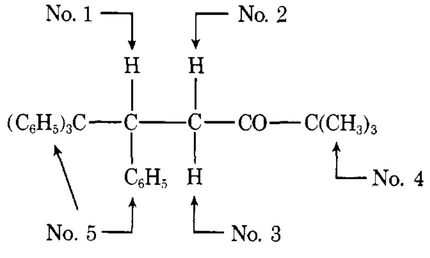
Reaction of Ph_3CLi with the Cis Enone 13. To a cold (0°) solution of 231 mg (1.38 mmol) of the enone **13** in 10 ml of DME was added, dropwise and with stirring, 3 ml of a DME solution containing 0.66 mmol of Ph_3CLi. As the resulting solution was stirred at 0°, the red color of the Ph_3C^- anion faded so that the solution was colorless after 15 min. The reaction mixture was partitioned between Et_2O and aqueous NH_4Cl and the Et_2O layer was washed with aqueous NaCl, dried, concentrated, and mixed with a known weight of n-$C_{12}H_{26}$ (an internal standard). Subsequent GLC analysis was performed on two different columns; each was calibrated with appropriate known mixtures of authentic samples. On one column (Carbowax 20*M* on Chromosorb P), the mixture was found to contain n-$C_{12}H_{26}$ (ret time 8.4 min), the cis enone **13** (10.8 min, 76% yield), and the trans enone **10** (12.4 min, 18% yield). On the second column (silicone SE-52 on Chromosorb P, temperature varied from 90-280° at 4°/min), the mixture was found to contain the trans enone **10** (ret time 8.8 min), the cis enone **13** (10.0 min), n-$C_{12}H_{26}$ (13.7 min), and Ph_3CH (41.4 min, 93% recovery); the mixture exhibited no GLC peak corresponding to the retention time (36.1 min) of the dihydro dimers derived[16] from enones **10** and **13.** When 1.5-ml aliquots of a DME solution, each containing 0.255 mmol of Ph$_3$CLi, were treated, dropwise and with stirring with a 0.064 *M* solution of the cis enone **13** in DME until the red color was just discharged, 0.256–0.269 mmol (1.00–1.05 equiv) of the enone **13** was required.

A solution of 480 mg (2.86 mmol) of the cis enone **13** in 20 ml of DME was treated, dropwise and with stirring during 2 min, with 25 ml of a DME solution containing, 5.0 mmol of Ph$_3$CLi. The resulting red solution was stirred for 5 min and then quenched with 5 ml of D$_2$O and subjected to the previously described work-up procedure. A portion of the crude residual product was separated by preparative TLC [silica gel, E. Merck GF-254, with Et$_2$O-pentane (2:98 v/v) as the eluent]. Samples of Ph$_3$CH (R_f 0.7), the cis enone **30** (R_f 0.5), and the trans enone **29** (R_f 0.3) were obtained for NMR analysis. Analysis of another aliquot of the crude product indicated that the enone mixture contained (GLC, Carbowax 20 *M* on Chromosorb P) 17% of the cis enone **30** (retention time 7.6 min) and 83% of the trans enone **29** (12.6 min). Collected (GLC) samples of these enones **29** and **30** were used for mass spectral and ir analyses. The cis enone **30** was obtained as a colorless liquid: NMR (CCl$_4$) δ 5.79 (1 H, 3 lines, $J_{\text{H-D}}$ = 2.0 Hz, β-vinyl CH) and 1.08 (18 H, s, *t*-Bu); mass spectrum, 3% d$_0$ species and 97% d$_1$ species. The trans enone **29** was obtained as a colorless solid, mp 41.5–43.5°, with ir and mass spectra corresponding to those of the previously described[16] sample: mass spectrum, 3% species, 95% d$_1$ species, and 2% d$_2$ species.

Reaction of Ph$_3$CLi with the Enone 11. To a solution of 300 mg (1.60 mmol) of the enone **11** in 20 ml of DME was added, dropwise and with stirring at 25°, a solution of 1.71 mmol of Ph$_3$CLi in 10.5 ml of DME. This was the minimum amount of Ph$_3$CLi solution required in order to maintain the red color of the Ph$_3$C$^-$ anion in the reaction solution. The resulting red solution was stirred at 25° for 5 min and then partitioned between Et$_2$O and aqueous NH$_4$Cl. After the ethereal solution had been washed with aqueous NaCl, dried, and concentrated, the residue was subjected to preparative TLC separation on a plate coated with silica gel (E. Merck, No. GF-254) employing an Et$_2$O-hexane mixture (1:20 v/v) as the eluent. The more rapidly eluted band (R_f 0.5) contained 197 mg of Ph$_3$CH (identified by comparison of TLC R_f values and ir spectra) and the slower moving band (R_f 0.25) contained (NMR analysis) the crude ketone **24.** This latter fraction was recrystallized from hexane to separate 671 mg (97%) of fractions of the ketone **24,** mp 134–139°. Recrystallization from hexane separated the pure ketone **24** as white plates: mp 137–139°; ir (CCl$_4$) 1705 cm^{-1} (C=O); uv (95% EtOH) shoulder at 238 mμ (ϵ 6110) with a series of weak maxima (ϵ less than 1000) in the range 258–273 mμ; NMR (CDCl$_3$) δ 6.5–7.6 (20 H, m, aryl CH), 5.38 (1 H, t, *J* = 6 Hz, benzylic CH), 2.95 (2 H, d, *J* = 6 Hz, CH$_2$CO), and 0.76 (9 H, s, *t*-Bu); mass spectrum, *m/e* (rel intensity) 245 (10), 244 (46), 243 (13), 167 (36), 166 (20), 165 (34), 131 (100), 105 (25), 103 (33), 77 (30), 45 (22), and 41 (26).

Anal. Calcd for C$_{32}$H$_{32}$O: C, 88.85; H, 7.46. Found: C, 88.85; H, 7.48.

A CCl$_4$ solution of the ketone **24** was treated with a series of aliquots of the NMR shift reagent, Eu(fod)$_3$. The relative rates at which various of the NMR proton signals were shifted downfield are indicated in the following structure with the proton labeled No. 1 undergoing the greatest shift and the protons labeled No. 5 undergoing the smallest shift. The mother liquors from recrystallization of the ketone **24** were examined by NMR [both with and without added Eu(fod)$_3$]. We could find no evidence for the presence of a second product structurally isomeric with the ketone **24.**



Reaction of Ph$_3$CLi with the Enone 9.[27] To a solution of 250 mg (1.20 mmol) of the enone **9** in 15 ml of DME was added, dropwise and with stirring during 3 min at 25°, a solution of 1.30 mmol of Ph$_3$CLi in 10 ml of DME. After approximately 75% of the Ph$_3$CLi solution had been added, the red color of the Ph$_3$C$^-$ anion persisted in the reaction solution for the remainder of the addition. The resulting red solution was stirred at 25° for 10 min and then partitioned between Et$_2$O and aqueous NH$_4$Cl. The solution was washed with aqueous NaCl, dried, and concentrated to leave a residual crude product that contained (TLC, E. Merck silica gel, GF-254, with an Et$_2$O-hexane mixture, 1:4 v/v, as the eluent) Ph$_3$CH (R_f 0.63) and the ketone **20** (R_f 0.36) with no starting material (R_f 0.45) being detected. The mixture was separated on comparable preparative TLC plates to give 365 mg of Ph$_3$CH (identified by comparison of TLC R_f values and ir spectra) and 435 mg (80%) of the crude ketone **20,** mp 158–164°. Recrystallization from an Et$_2$O-hexane mixture afforded the pure ketone **20** as white needles: mp 167–168.5°; ir (CHCl$_3$) 1686 cm^{-1} (conjugated C=O); uv maximum (95% EtOH) 241 mμ (ϵ 19,000); NMR (CDCl$_3$) δ 6.6–7.8 (25 H, m, aryl CH), 5.64 (1 H, t, *J* = 6 Hz, benzylic CH), and 3.48 (2 H, d, *J* = 6 Hz, CH$_2$CO); mass spectrum, *m/e* (rel intensity) 281 (3), 244 (22), 243 (100), 242 (25), 208 (40), 207 (44), 182 (20), 167 (62), 166 (30), 165 (68), 104 (20), 103 (98), 94 (30), 78 (25), 77 (81), 51 (34), and 43 (23).

Anal. Calcd for C$_{34}$H$_{28}$O: C, 90.23; H, 6.24. Found: C, 90.01; H, 6.30.

Reaction of Ph$_3$CLi with the Enone 12. To a solution of 363 mg (1.93 mmol) of the enone **12** in 10 ml of DME was added, dropwise and with stirring during 3 min, 8.8 ml of a DME solution containing 1.94 mmol of Ph$_3$CLi. During this addition the red color of Ph$_3$C$^-$ persisted in the solution after approximately 50% (0.5 equiv) of the Ph$_3$CLi had been added. The resulting red solution was stirred for 15 min and then partitioned between Et$_2$O and aqueous NH$_4$Cl. The organic solution was washed with aqueous NaCl, dried, and concentrated to leave a crude residual product that was subjected to preparative TLC [silica gel, E. Merck GF-254, with an Et$_2$O-hexane mixture (1:20 v/v) as eluent]. The components separated were 310 mg of Ph$_3$CH (R_f 0.9, identified by ir analysis), 79 mg (22% recovery) of the starting enone **12** (R_f 0.75, identified by NMR analysis), 188 mg (23%) of the crude monomeric product **25** (R_f 0.7), and 556 mg of a series of more slowly eluted components (R_f 0.1–0.4) that appeared (ir and NMR analyses) to be low molecular weight polymeric materials similar to structures **22a** and/or **22b.** The crude monomeric product **25** (contaminated with the starting enone **12,** NMR analysis) was recrystallized repeatedly from hexane to separate 30 mg of the pure ketone **25** as white needles: mp 131–133°; ir (CHCl$_3$), 1685 cm^{-1} (conjugated C=O); uv maximum (hexane) 224 mμ (ϵ 24,900) with a shoulder at 241 mμ (ϵ 8600); NMR (CDCl$_3$) δ 6.8–7.9 (19 H, m, aryl CH), 5.48 (1 H, s, Ar$_3$CH), 3.1–3.6 (3 H, m, CH$_2$CO and benzylic CH), and 0.93 (9 H, s, *t*-Bu); mass spectrum, *m/e* (rel intensity) 279 (7), 243 (1), 167 (17), 150 (16), 149 (100), 138 (17), 71 (23), 70 (27), 57 (40), 56 (24), 55 (29), 43 (29), and 41 (40).

Anal. Calcd for C$_{32}$H$_{32}$O: C, 88.85; H, 7.46. Found: C, 89.02; H, 7.49.

A solution of 200 mg (1.1 mmol) of PhCOPh in 5 ml of DME was treated with 10 ml of a DME solution containing 2.0 mmol of Ph$_3$CLi. The red color of the Ph$_3$C$^-$ anion persisted after the addition of several drops of the Ph$_3$CLi solution and remained while the solution was stirred for 4 hr at 25°. The resulting red solution was partitioned between Et$_2$O and aqueous NH$_4$Cl and the organic layer was washed with aqueous NaCl and then dried and concentrated. Analysis (NMR and TLC) of the crude product indicated the presence of only PhCOPh and Ph$_3$CH. Separation by preparative TLC (silica gel, E. Merck PF-254, with an Et$_2$O-hexane eluent, 1:20 afforded 403 mg (83%) of Ph$_3$CH (R_f 0.5) and (v/v) 185 mg (93%) of PhCOPh (R_f 0.2). Both products were identified by ir analysis.

Reaction of Me$_2$CuLi with the Enone 12. To a cold (0°) solution of Me$_2$CuLi, obtained from 350 mg (1.84 mmol) of CuI and 2.98 mmol of MeLi in 12 ml of Et$_2$O, was added a solution of 194 mg (1.03 mmol) of the enone **12** in 2 ml of Et$_2$O. The resulting mixture, which exhibited a transient red color followed by separation of (MeCu)$_n$ as a yellow solid, was stirred for 30 min at 0° and then partitioned between Et$_2$O and aqueous NH$_4$Cl. The ethereal solution was washed with aqueous NaCl, dried, and concentrated to leave 188 mg (89%) of the crude ketone **14** (ir and NMR analysis) that exhibited a single GLC peak (Carbowax 20 *M* on Chromosorb P), retention time 12.4 min. A collected (GLC) sample of the pure ketone **26** was obtained as a colorless liquid: $n^{25}\text{D}$ 1.5081; ir (CCl_4), 1690 cm^{-1} (conjugated C=O); uv maxima (95% EtOH) 239.5 (ϵ 11,700) and 277 mμ (ϵ 1090); NMR (CCl_4) δ 7.2–8.0 (5 H, m, aryl CH), 2.3–3.2 (2 H, m, CH_2CO), 1.7–2.2 (1 H, m, CH), 0.92 (9 H, s, *t*-Bu), and 0.85 (3 H, d, J = 7 Hz, CH_3); mass spectrum, *m/e* (rel intensity) 204 (M^+, 16), 148 (31), 147 (78), 133 (28), 120 (53), 105 (100), 77 (56), 57 (32), 43 (34), and 41 (21).

Anal. Calcd for $C_{14}H_{20}O$: C, 82.30; H, 9.87. Found: C, 82.28; H, 9.92.

Electrochemical Measurements. The polarographic and cyclic voltammetry measurements employed a custom-made polarographic module utilizing solid-state amplifiers that followed the typical three-electrode design. Descriptions of the cells, working electrodes, and reference electrodes were described previously[28] along with the purification procedures used for $n\text{-}Bu_4NBF_4$ and DMF. The solvent, DME, was purified by distillation from $LiAlH_4$ and commercial $LiClO_4$ (Alfa Inorganics) was purified by recrystallization from anhydrous DME (ca. 60 g of salt in 85 ml of solvent) to separate the complex, $LiClO_4(CH_3OCH_2CH_2OCH_3)_2$, as white needles. All polarographic measurements were determined at a dropping Hg electrode with solution in DMF containing 0.5 *M* $n\text{-}Bu_4NBF_4$. The cyclic voltammetry measurements were determined with a spherical bare Pt electrode in either DMF containing 0.5 *M* $n\text{-}Bu_4NBF_4$ or in DME containing 0.15–0.17 *M* $LiClO_4$. The measurements in the DME–$LiClO_4$ solution with a Pt electrode were limited to potentials less negative than the −2.0 V vs. SCE because the background current became excessive at more negative potentials.

Solutions of Ph_3CLi and Ph_2CHLi for use in these measurements were obtained by reaction of DME solutions of MeLi with an excess of either Ph_3CH or Ph_2CH_2. After these solutions had been standardized by titration to a colorless end point with *sec*-BuOH,[24] aliquots were added to the DME–$LiClO_4$ solution in an electrochemical cell. A solution of the sodium enolate **7** in DME was obtained by reaction of $PhCH_2COCH_3$ with excess NaH in DME[7a] and a solution of $(EtO_2C)_2CH^-Na^+$ in DMF was similarly prepared by reaction of $(EtO_2C)_2CH_2$ with excess NaH in DMF. These latter solutions of sodium enolates were standardized by quenching aliquots in a known excess of standard aqueous HCl followed by titration to a phenolphthalein end point with standard aqueous NaOH.

The $E_{1/2}$ values and estimated half-lives of radical intermediates, summarized in Table I and Scheme I, were determined by previously described procedures.[16,28] In cyclic voltammetry studies of the oxidation of carbanionic intermediates (Table I), for cases where no reduction peak was observed during the reverse scan, the $E_{1/2}$ value was estimated by measuring the potential value where the anodic current was 85% of its peak value.[29] To obtain a comparison of $E_{1/2}$ values measured in the DMF–ammonium salt solution and in the DME–$LiClO_4$ solution, the $E_{1/2}$ value for enone **11** (0.011 *M*) (previously determined[16] to be −1.698 V vs. SCE in DMF containing $n\text{-}Pr_4NClO_4$) was measured at a spherical Pt electrode in DME containing 0.2 *M* $LiClO_4$ and found to be −1.72 V vs. SCE. Although the $E_{1/2}$ values were comparable in the two solutions of the enone **11**, the half-life of the derived radical anion was much shorter ($<10^{-2}$ sec) in the DME–$LiClO_4$ solution as would be expected from previous observations of the effect of added Li^+ cation.[16]

The electrochemical reduction of a solution of Ph_2CO (**14**, 0.005–0.012 *M*) in DMF containing 0.5 *M* $n\text{-}Bu_4NBF_4$ was examined by polarography and cyclic voltammetry. The solution exhibited two reduction waves with $E_{1/2}$ values of −1.80 V vs. SCE (n = 1.0, i_d = 27–54 μA) and −2.34 V vs. SCE (n = 1.2, i_d = 21–34 μA);[30] the first reduction wave was a reversible process (half-life > 10 sec) but the second wave was not.

References and Notes

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

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(23) 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 spectrometer and the ^{13}C NMR spectra were obtained at 100 mHz with a JEOL Fourier transform spectrometer, Model PFT-100. The chemical shift values are expressed in δ values (ppm) relative to a Me_4Si internal standard. The mass spectra were obtained with an Hitachi (Perkin-Elmer), Model RMU-7, or a Varian, Model M-66, mass spectrometer. All reactions involving strong bases or reactive organometallic intermediates were performed under a nitrogen atmosphere.

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