Reactions Involving Electron Transfer. I. Reduction of 2,2,6,6-Tetramethyl-4-hepten-3-one[1]

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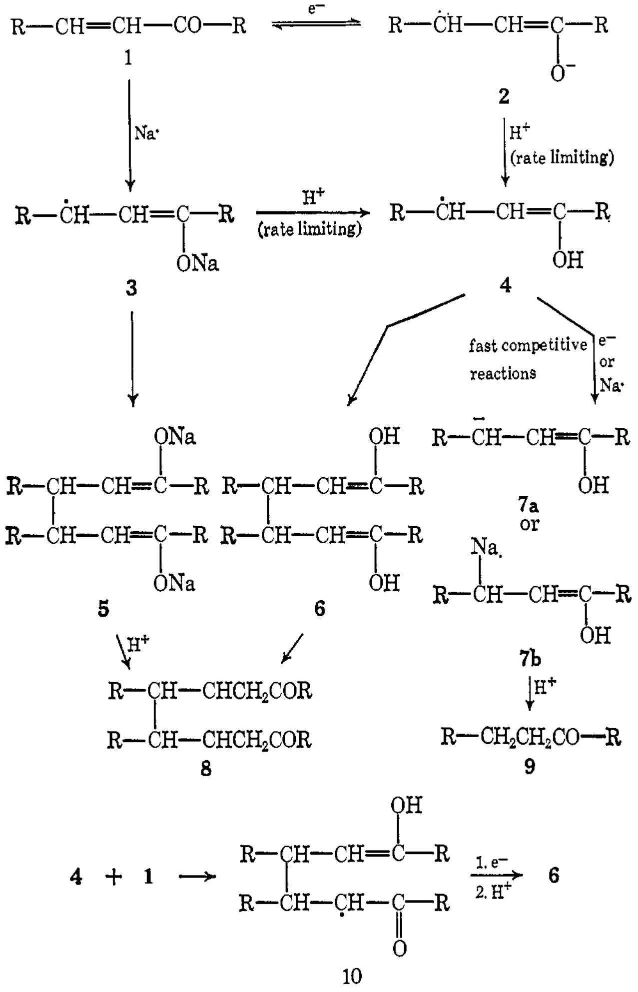
Abstract: The polarographic reduction potentials and the half-lives of the initial radical anion reduction products have been measured for a representative group of α,β-unsaturated ketones. In dipolar aprotic media (DMF, HMP) the radical anion **16** derived from 2,2,6,6-tetramethyl-*trans*-4-hepten-3-one (**11**) has a sufficiently long half-life (*ca.* 10 min) to permit measurement of its properties. The lifetime of this radical anion **16** is markedly lowered by the presence of proton donors, lithium cation, or oxygen in the reaction medium. In the presence of proton donors or metal cations, this radical anion **16** is rapidly converted to a racemic dihydrodimer **24**. Evidence is presented for two geometrically isomeric radical anions **17** and **16** being formed by reduction of the *cis* (**14**)- and *trans* (**11**)-enones. However, one of the isomeric anion radicals is rapidly converted to the other more stable isomer believed to be **16**. Epr measurements have demonstrated the occurrence of electron exchange between the radical anion and the corresponding unreduced enone. The epr measurements also suggest that 40–50% of the unpaired electron density of the radical anion **16** is located at the β-carbon atom with little or no unpaired spin density at the α-carbon atom. The properties of solutions of sodium in hexamethylphosphoramide (HMP) have been examined and reduction of the geometrically isomeric tetramethylheptenones **11** and **14** with sodium in HMP have been studied. In HMP solution either the monomeric (**25**) or dimeric (**24**) reduction product could be made to predominate by the choice of reaction conditions. Under appropriate reaction conditions the dimerization process was at least partially stereospecific with the racemic dimer **24** being formed from the *trans*-enone **11** and mainly the *meso*-dimer **30** being formed from the *cis*-enone **14**.

A useful classification divides organic redox reactions into either (1) reactions in which one or more atoms is transferred in each step of the reaction path (*e.g.*, metal hydride reductions) or (2) reactions in which one or more steps in the reaction path involves only the transfer of an electron (*e.g.*, reductions with dissolving metals). In this paper and subsequent publications in this series we will describe our investigations of redox reactions involving at least one electron-transfer step. The purpose of our investigations is twofold; we wish both to gain a better understanding of the reaction paths and the properties of intermediates in these redox reactions and also to explore the possible use of reaction intermediates formed by electron transfer (*e.g.*, anion radicals or cation radicals) as reactive intermediates in other synthetically useful processes such as C–C bond formation.

The program has been initiated[3] with a study of the reduction of α,β-unsaturated ketones by the addition of electrons from a suspension of alkali metal, from a solution of an alkali metal, or from a mercury cathode in an electrolysis cell. As a result of these studies we believe the principal reaction paths followed with aliphatic enones under the conditions of our work are illustrated in Scheme I. The results of our work and other studies[4] leave little doubt that the initial

Scheme I



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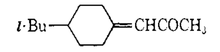
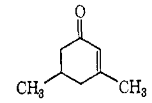
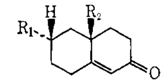
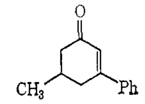
(2) (a) National Institutes of Health Predoctoral Fellow, 1966–1969; (b) author to whom inquiries should be addressed.

(3) For Part II see H. O. House, R. W. Giese, K. Kronberger, J. P. Kaplan, and J. F. Simeone, *J. Amer. Chem. Soc.*, **92**, 2800 (1970).

(4) (a) C. L. Perrin, *Progr. Phys. Org. Chem.*, 3, 165 (1965); (b) P. Zuman, D. Barnes, and A. Ryvolova-Kejharova, *Discussions Faraday Soc.*, **45**, 202 (1968); (c) H. Smith, "Organic Reactions in Liquid

Table I. Polarographic Half-Wave Potentials for the Reduction of Representative α,β-Unsaturated Ketones in DMF Solution Containing 0.1–0.4 *M* *n*-Pr_4NClO_4

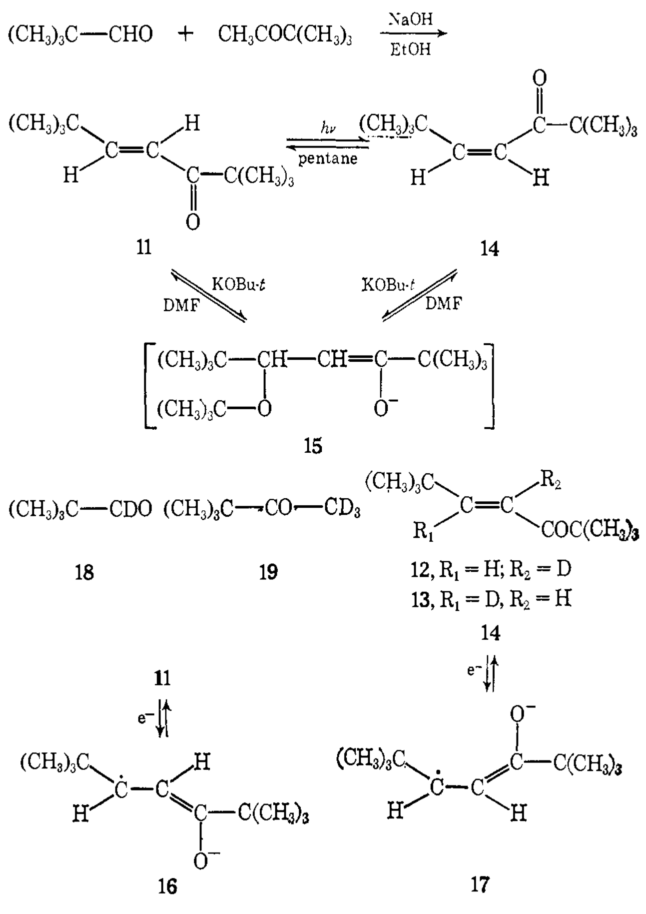
Compound	Temp, °C	$E_{1/2}$, V (*vs.* sce) Wave 1	$E_{1/2}$, V (*vs.* sce) Wave 2	Δ*E*/log ($i/i_d - i$), mV
trans-t-BuCH═CHCOBu-*t* **11**	28	−2.224		61
	28	-1.995^a		60
	28	-1.91^b		
cis-t-BuCH═CHCOBu-*t* **14**	28	−2.207		61
	25–27	−2.12		
	25–27	−2.22		
 $R_1 = R_2 = H$	25–27	−2.15		
R_1 = *t*-Bu; R_2 = H	25–27	−2.15		
R_1 = H; R_2 = CH_3	25–27	−2.10		
trans-PhCH═CHCOBu-*t*	28	−1.698	−2.255	53 and 56
cis-PhCH═CHCOBu-*t*	28	−1.710	−2.234	52 and 85
trans-PhCH═CHCOCH$_3$	25–27	−1.64	−2.61	
	25–27	-1.52^c	-2.01^c	
	25–27	-1.50^d	-1.93^d	
	25–27	−1.71		
	25–27	-1.67^c	-2.04^c	
trans-t-BuCH═CHCOPh	25–27	−1.69	−2.38	

[a] Contains 10% of an aqueous buffer, pH ~13. [b] Contains 10% of an aqueous buffer, pH ~9. [c] Contains 5% water. [d] Contains 5% CF_3CH_2OH.

reduction steps for aliphatic enones involve the successive addition of an electron (or a metal atom) and a proton to form the allylic radical **4**. However, certain ambiguities still exist in the fast steps following the rate-limiting formation of **4** which lead to dimeric (**8**) or monomeric (**9**) reduction products.

Selection and Preparation of the Starting Enones. For our initial study, we required an enone **1** which could be converted to a relatively stable anion radical **2**. However, we wished to avoid an enone with conjugating substituents (*e.g.*, aryl groups) which would be likely to complicate epr study and would also possess potential reaction sites at locations other than within the enone system.[5] It is also questionable whether a system with extended conjugation is a valid model for study of a reduction reaction which finds its major synthetic utility with aliphatic enones. After preliminary experimentation, we selected the tetramethylheptenone system **11** as a suitable candidate for detailed study. This *trans*-enone **11** and its monodeuterio derivatives **12** and **13** could be prepared (Scheme II) by conventional methods.[6] Furthermore, the stereoisomeric *cis*-enone **14**

Scheme II



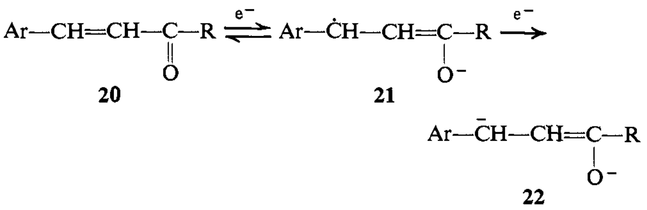
Ammonia," Interscience Publishers, Inc., New York, N. Y., 1963, pp 142–147; (d) F. D. Popp and H. P. Schultz, *Chem. Rev.*, **62**, 19 (1962); (e) M. J. Allen, "Organic Electrode Processes," Reinhold Publishing Corp., New York, N. Y., 1958; (f) P. Angibeaud, M. Larchevêque, H. Normant, and B. Tchoubar, *Bull. Soc. Chim. Fr.*, 595 (1958); (g) P. Martinet and J. Simonet, *ibid.*, 3533 (1967); (h) G. Stork, P. Rosen, and N. L. Goldman, *J. Amer. Chem. Soc.*, 83, 2965 (1961); (i) G. Stork and S. D. Darling, *ibid.*, **86**, 1761 (1964); (j) M. J. Weiss and coworkers, *Tetrahedron*, 20, 357 (1964); (k) M. J. T. Robinson, *ibid.*, 21, 2475 (1965); (l) M. Fetizon and J. Gore, *Tetrahedron Lett.*, 471 (1966); (m) S. D. Malhotra, D. F. Moakley, and F. Johnson, *ibid.*, 1089 (1967); (n) H. A. Smith, B. J. L. Huff, W. J. Powers, III, and D. Caine, *J. Org. Chem.*, **32**, 2851 (1967); (o) M. M. Bazier, J. D. Anderson, J. H. Wagenknecht, M. R. Ort, and J. P. Petrovich, *Electrochim. Acta*, **12**, 1377 (1967); (p) S. Wawzonek and A. Gundersen, *J. Electrochem. Soc.*, **111**, 324 (1964).

(5) For example, reaction of benzophenone ketyl with CH_3I yielded products in which a methyl group was located not only at the original carbonyl group but also at the *o* and *p* positions of the phenyl ring; G. O. Schenck and G. Matthias, *Tetrahedron Lett.*, 699 (1967).

could be obtained from the *trans*-isomer **11** by photoisomerization. Reaction of the less stable *cis*-enone **14** with KOBu-*t* in dimethylformamide (DMF) led to equilibration presumably by the reversible addition of the alkoxide to form the intermediate β-alkoxy ketone **15**. Since the *trans*-enone **11** obtained from this equilibration at 27° contained less than 0.1% of the *cis*-isomer **14**, the free energy difference between the *cis*- and *trans*-isomers **11** and **14** in DMF solution at 27° is greater than 4 kcal/mol.

The comparable intensities of infrared absorption corresponding to the the C=C and C=O stretching vibrations in the starting ketone **11** indicate that this material exists predominantly in the cisoid conformation illustrated in structure **11**.[7] We assume that corresponding conformations (indicated in structures **14**, **16**, and **17**) are also probable for the *cis*-enone and the derived radical anions since only such conformations allow the enone system to remain planar without a serious steric interaction between either two *t*-butyl groups or one *t*-butyl group and the β-hydrogen atom.

Transfer of an Electron to an Enone by Electrolysis. To explore the effect of structure on the ease of addition of an electron to an α,β-unsaturated ketone a representative group of enones (see Table I) were reduced in dimethylformamide (DMF) solution by conventional polarographic techniques employing a dropping mercury electrode and tetra-*n*-propylammonium perchlorate (n-Pr_4NClO_4) as the supporting electrolyte. The polarographic half-wave reduction potentials ($E_{1/2}$) were measured at 25–28° with respect to a saturated calomel electrode (sce) as a reference. As has been noted in earlier studies,[4a,b,g,p] in anhydrous media enones without additional conjugating substituents exhibit a single one-electron reduction wave in the region (0 to −2.7 V) accessible for measurement; the variation in $E_{1/2}$ values (−2.10 to −2.22 V) was *ca.* 0.1 V. The presence of a phenyl substituent at either end of the enone system lowered the value of the first reduction wave (−1.64 to −1.71 V) by *ca.* 0.5 V[8] and generally permitted the observation of a second reduction wave ($E_{1/2}$ −2.23 to −2.61 V) at a potential 0.5–1.0 V more negative. These two reduction waves observed with aryl-substituted enones **20** are usually attributed[4a,b] to the successive reductions to the anion radical (**20** → **21**) and to the dianion (**21** → **22**). The less negative potential (*ca.* 0.5 V or 12 kcal/mol)[8] for the first reduction step is attributable to the ability of the aryl-substituted anion radical **21** to distribute the extra electron added to the antibonding π orbital over a larger volume than would be possible with an aliphatic anion radical. This increased possibility for electron delocalization and the attendant lowering of unfavorable electronic interactions also accounts for the ability of aryl-substituted anion radicals **21** to accept an additional electron forming dianion **22**. The formation of an analogous dianion from an aliphatic enone would be expected to require a reduction potential more negative than −3.0 V (*vs.* sce).[9] Since reduction potentials of this negative are normally not obtainable either by electrolysis with the subsequently discussed solutions of metals, we believe that *free dianion intermediates are seldom if ever involved in reductions of aliphatic enones by processes incorporating electron-transfer steps.*



$$\mathrm{Ar{-}CH{=}CH{-}\underset{\underset{\displaystyle O}{\|}}{C}{-}R} \overset{e^-}{\rightleftharpoons} \mathrm{Ar{-}\dot{C}H{-}CH{=}\underset{\underset{\displaystyle O^-}{|}}{C}{-}R} \xrightarrow{e^-} \mathrm{Ar{-}\overset{-}{C}H{-}CH{=}\underset{\underset{\displaystyle O^-}{|}}{C}{-}R}$$

20 **21** **22**

Accurate values of $E_{1/2}$ for the reductions of the *cis*- and *trans*-enones **14** and **11** were of interest because of their relation to the geometry of the radical anions **16** and/or **17**. Since the formation of these radical anions involves addition of an electron to an antibonding π orbital in the enone system, the question exists whether an acyclic radical anion will have lower energy as one of the geometrically isomeric planar structures such as **16** or **17** or as a common nonplanar structure which minimizes interaction between the partially filled antibonding orbitals. Since the two geometrically isomeric enones **11** and **14** differ in free energy by more than 4 kcal/mol (or equivalently 170 mV/mol), if these enones were being reduced to a common nonplanar anion radical their reduction potentials would differ by at least 170 mV. In fact, polarographic measurement under conditions where the *cis*-isomer **14** was not being isomerized to the *trans*-isomer **11** demonstrated that the reduction potentials of the two enones (Table I) differed by only 17 mV. Consequently, we conclude that each enone **11** or **14** is reduced to a different anion radical which we believe to possess one of the two planar structures **16** or **17**. However, subsequently described epr measurements and reductions with metal solutions indicate that equilibration of the initially formed geometrical isomers **16** and **17** is relatively rapid. Presumably the barrier to rotation about the α,β-C-C bond of the enone is lowered substantially when the antibonding π orbital is populated to form the anion radical.

Epr Spectra of the Radical Anion. When solutions of either the *cis*- or *trans*-ketones **14** or **11** in DMF containing n-Bu_4NClO_4 were electrolyzed at 25–30° in the probe of an epr spectrometer, a well-resolved spectrum of an anion radical was obtained (Figure 1, spectra A and D). The fact that the same spectrum was obtained from either isomeric ketone, taken with previously cited polarographic evidence, suggests that the anion radicals **16** and **17** initially formed are rapidly equilibrated to give a solution which contains primarily one anion radical. From consideration of the nonbonded steric interactions present in **16** and **17**, it seems highly probable that the *trans*-anion radical **16** is the predominant species present. Support for these hypotheses was gained from our subsequently described study of the hydrodimerization products and from a partial electrolysis of the *cis*-enone **14** on a

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(6) Very brief descriptions of the unsaturated ketone **11** have been published: (a) K. Dimroth and W. Mach, *Angew. Chem.*, **80**, 489, 490 (1968); (b) W. Rundel and K. Besserer, *Tetrahedron Lett.*, 4333 (1968).

(7) (a) R. L. Erskine and E. S. Waight, *J. Chem. Soc.*, 3425 (1960); A. J. Bowles, W. O. George, and W. F. Maddams, *ibid.*, *B*, 810 (1969).

(8) For a process involving the transfer of one electron per molecule, a potential difference of 1.00 V corresponds to an energy difference of 23.06 kcal/mol.

(9) The estimate of a minimum reduction potential of −3.0 V (*vs.* sce) is based on the fact that even with aryl-substituted anion radicals which permit extensive electron delocalization of $E_{1/2}$ value for the second reduction step is about 1 V more negative than the potential required to produce the radical anion.

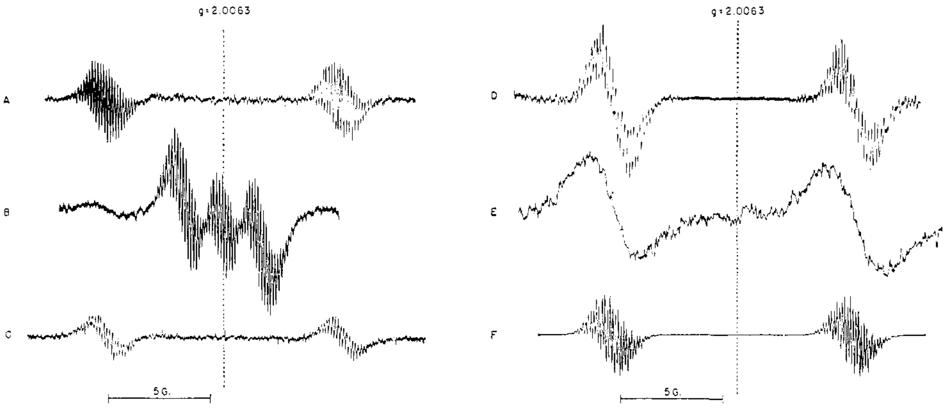

Figure 1. Epr spectra from: (A) electrolytic reduction of **11** in DMF; (B) electrolytic reduction of **13** in DMF; (C) electrolytic reduction of **12** in DMF; (D) electrolytic reduction of **14** in DMF; (E) reaction of **11** with Na-K in DME; (F) computer simulation of spectrum A.

preparative scale which resulted in conversion of the *cis*-enone **14** to the *trans*-isomer **11** in the electrolysis cell.

The proton responsible for the major hyperfine splitting ($a_{\mathrm{H}} = 11.67$ G) observed in these epr spectra was identified by measuring the spectra of the corresponding monodeuterated ketones **12** and **13**. As illustrated in Figure 1 (spectra A, B, and C), substitution of deuterium for the β-hydrogen atom (spectrum B from **13**) changed the major hyperfine splitting from a doublet ($a_{\mathrm{H}} = 11.67$ G) to a triplet ($a_{\mathrm{D}} = 1.75$ G, calcd 1.79 G). Interestingly, substitution of deuterium for the α-hydrogen atom gave a spectrum (spectrum C for **12**) which was essentially identical with the spectrum of the nondeuterated ketone **11**. The entire spectrum could be simulated (spectrum F) by assuming hyperfine coupling values of 11.67 and 0 G for the β- and α-hydrogen atoms with 0.27 G for the nine protons of one *t*-butyl group and 0.39 G for the nine protons of the other *t*-butyl group.

Assuming that the radical anion **16** is planar, the principal hyperfine coupling constant ($a_{\mathrm{H}} = 11.67$ G) observed suggests[10] that about 40–50% of the unpaired electron density in this radical anion is located at the β-carbon atom. The bulk of the remaining odd electron density is apparently located at the carbon and oxygen atoms of the carbonyl group with little if any unpaired electron density at the α-carbon atom. Although an epr spectrum (Figure 1, spectrum E) with similar gross features was obtained when the *trans*-ketone **11** was treated with Na-K alloy in 1,2-dimethoxyethane (DME), we were unable to obtain a sufficiently well-resolved spectrum to permit a definite conclusion about the paramagnetic species present.

Our hyperfine splitting constants are in reasonable agreement with the values found for the anion radicals from simple ketones such as di-*t*-butyl ketone ($a_{\beta\mathrm{H}} = 0.12$ G),[11] *t*-butylisopropyl ketone ($a_{\alpha\mathrm{H}} = 2.38$ G, $a_{\beta\mathrm{H}} = 0.1$ G),[11] dicyclopropyl ketone ($a_{\alpha\mathrm{H}} = 3.5$ G),[12] pinacolone ($a_{\alpha\mathrm{H}} = 15.05$ G, $a_{\beta\mathrm{H}} = 0.04$ G),[13] and acetone ($a_{\alpha\mathrm{H}} = 16.4$ G)[14] and di-*t*-butyl-1,2-ethanedione ($a_{\beta\mathrm{H}} = 0.28$–$0.29$ G).[16] To our knowledge only one group has reported[17] obtaining the epr spectrum of an aliphatic enone anion radical obtained by treatment of 4,4-dimethylcyclohex-2-en-1-one with potassium in liquid NH_3 at −60°. These authors reported the hyperfine splitting constants to be: $a_{\alpha\mathrm{CH}_2} = 5.87$ G, $a_{\mathrm{vinyl\ CH}} = 5.16$ G, and $a_{\mathrm{vinyl\ CH}} = 1.72$ G. No other experimental evidence was offered either to establish the validity of these assignments or to establish which vinyl proton gives rise to the larger splitting constant.

Transfer of an Electron from Sodium Metal to an Enone. The studies described in this paper used sodium metal either suspended in tetrahydrofuran (THF) or dissolved in hexamethylphorphoramide (HMP)[18] or a HMP–THF mixture. Although these blue solutions have properties similar to solutions of the alkali metals in liquid NH_3 or low molecular-weight amines,[19]

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[10] J. R. Bolton, "Radical Ions," E. T. Kaiser and L. Kevan, Ed., Interscience Publishers, Inc., New York, N. Y., 1968, pp 1–33.

[11] (a) N. Hirota and S. I. Weissman, *J. Amer. Chem. Soc.*, **82**, 4424 (1960); **83**, 3533 (1961); **86**, 2537, 2538 (1964); (b) N. Hirota, *ibid.*, **89**, 32 (1967); (c) V. M. Kazakova and Ya. K. Syrkin, *Zh. Strukt. Khim.*, **3**, 536 (1962).

[12] G. A. Russell and H. Malkus, *J. Amer. Chem. Soc.*, **89**, 160 (1967).

[13] P. R. Jones and R. West, *ibid.*, **90**, 6978 (1968).

[14] J. E. Bennett, B. Mile, and A. Thomas, *J. Chem. Soc., A*, 298 (1968). In this study composite spectra or spectra which changed with time at 77–140°K were observed in a number of cases. These changes of composite spectra were suggested to arise from reaction of the initially formed ketyl with the excess ketone in the frozen matrix to form α-keto radicals.[15]

[15] The epr spectra of α-keto radicals derived from 1,3-dicarbonyl compounds have been described by G. A. Russell and J. Lokensgard, *J. Amer. Chem. Soc.*, **89**, 5059 (1967). The observation that the hyperfine coupling constants for the groupings $H\dot{C}R_2$ or $CH_3\dot{C}R_2$ have very similar values when R = CH_3 or COR′ is suggested to mean that the unpaired electron is primarily located at the α-carbon atom (*i.e.*, i) with little delocalization into the carbonyl group (*i.e.*, ii).


i ii

[16] (a) G. A. Russell, *et al.*, *Rec. Chem. Progr.*, **27**, 3 (1966); (b) H. C. Heller, *J. Amer. Chem. Soc.*, **86**, 5346 (1964).

[17] H.-L. J. Chen and M. Bersohn, *Mol. Phys.*, **13**, 573 (1967).

[18] Previous discussions of the properties of hexamethylphosphoramide and solutions of alkali metals in this solvent are given by (a) H. Normant, *Angew. Chem. Intern. Ed. Engl.*, **6**, 1046 (1967); (b) H. Normant, *Bull. Soc. Chim. Fr.*, 791 (1968); (c) H. Normant, T. Cuvigny, J. Normant, and B. Angelo, *ibid.*, 3441 (1965); (d) G. Fraenkel, S. H. Ellis, and D. T. Dix, *J. Amer. Chem. Soc.*, **87**, 1406 (1965); (e) H. L. J. Chen and M. Bersohn, *ibid.*, **88**, 2663 (1966); (f) M. Szwarc, *Progr. Phys. Org. Chem.*, **6**, 323 (1968).

[19] For recent reviews and leading references, see (a) M. C. R. Symons, *Quart. Rev.* (London), **13**, 99 (1959); (b) R. Catterall and M. C. R. Symons, *J. Chem. Soc., A*, 13 (1966); (c) R. Catterall, M. C. R. Symons, and J. W. Tipping, *ibid.*, 1234 (1967); (d) U. Schindewolf, *Angew. Chem. Intern. Ed. Engl.*, **7**, 190 (1968); (e) J. L. Dye, *Accounts Chem. Res.*, **1**, 306 (1968).

relatively concentrated (0.5 M) solutions of Na in pure HMP tend to decompose with loss of the blue color after standing a few minutes at 0–25°. However, the stability of these Na–HMP solutions can be markedly enhanced by the addition of various apparently inert cosolvents.[18c] In our work THF was a particularly convenient cosolvent; its use allowed us to prepare solutions 0.2–0.35 M in sodium with mixtures of HMP and THF which could be standardized by titration with 2-butanol or pinacolone to a colorless end point. These solutions could be stored at 0–25° for periods of hours without decomposition and, by proper choice of concentrations, it was possible to cool these solutions to temperatures as low as $-78°$ without the solutions freezing. Although the blue color of the solutions was discharged very rapidly by the addition of oxygen, water, or a primary alcohol (*e.g.*, MeOH, EtOH), the blue solutions persisted for periods of 1 hour or more at 0° after the addition of tertiary alcohols such as *t*-BuOH or Et_3COH.[20] The stability of Na-HMP solutions in the presence of secondary alcohols was intermediate between these two extremes.

In agreement with the studies of Normant[18a–c] and of Fraenkel,[18d] we observed only a single sharp epr signal ($g = 2.0022$) for various samples of these blue solutions of Na either in pure HMP or in HMP–THF mixtures. At no time did we observe the complex hyperfine splitting pattern reported[18e] for solutions of sodium in HMP which had been allowed to decay until a very low concentration of a paramagnetic species was present. Although Chen and Bersohn attributed their observed spectrum to the presence of unpaired electrons tightly solvated by ten HMP molecules, we note that their published spectrum bears a remarkable resemblance to the epr spectrum of the naphthalene anion radical and believe their interpretation open to question.

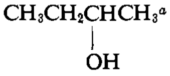
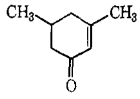
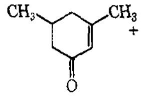
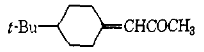
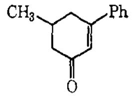
From comparison of intensity measurements with a solution containing a known concentration of diphenylpicrylhydrazyl, we found a solution containing 0.5 M sodium in an HMP–THF mixture (2:1 v/v) at 25–30° to be 1.4×10^{-3} M in species with unpaired electrons. This value is similar to the 10^{-3} M concentration of unpaired electrons found for solutions of alkali metals in liquid ammonia[19d] and suggests that in HMP like liquid ammonia at metal concentrations of 10^{-2} M or greater most of the solvated electrons present are either paired or associated in larger aggregates. The fact that we could easily obtain sharp nmr signals with the same chemical shift values as pure HMP for the protons of the HMP solvent in these blue solutions is also consistent with the idea that the concentration of paramagnetic species is relatively low.[21]

The potential developed between a platinum electrode and a saturated calomel electrode in electrical contact with a Na–HMP solution at 28° was -2.96 V. Values of -2.2 to -2.3 V (*vs.* sce) have been reported for solutions of sodium in liquid ammonia at $-33°$.[22]

Our observed potential (E *vs.* E_{ref}), like the potential of solutions of sodium in liquid ammonia,[22c] was relatively independent of the dissolved sodium concentration in the range 10^{-2}–0.3 M.

When aliquots of standard blue solutions of sodium in HMP–THF mixtures were treated with various substances (Table II), the number of moles of material required to discharge the blue color provided a measure of the average number of electrons which were consumed by each molecule of the substrate added to the alkali metal solution. Approximately one electron per molecule was consumed by 2-butanol, pinacolone, isophorone, 4-*t*-butylcyclohexylidenacetone, and the *trans*-ketone **11** (at $-35°$) whereas benzil accepted two electrons per molecule to form the red dianion.[23] Several β-phenyl α,β-unsaturated ketones examined consumed between one and two electrons per molecule.

Table II. Titrations Employing Standardized Solutions of Sodium in HMP–THF Mixtures at 25°

Compd	Mol of compd required per g-atom of Na (color of solution at end point)
 $CH_3CH_2CH(OH)CH_3$[a]	1.1 (colorless)
Ph—CO—CO—Ph[b]	0.50 (red)[c]
	1.1 (yellow)
 1.5 equiv of Et_3COH	0.46 (yellow)
	0.97 (yellow)
trans-*t*-Bu—CH═CHCO-Bu-*t*	0.67 at 25° (yellow) 0.79 at $-35°$ (yellow)
trans-PhCH═CHCOBu-*t*	0.67 (red)
trans-PhCH═CHCOPh	0.67 (red)
	0.37 (red)

[a] Added as a solution in xylene. [b] Added either as a pure solid or as a solution in HMP. [c] The radical anion of benzil is blue while the dianion is red. See N. L. Bauld, *J. Amer. Chem. Soc.*, **87**, 4788 (1965).

The data obtained with alkyl-substituted α,β-unsaturated ketones were complicated by the ability of the initially formed anion radicals **2** or **3** to abstract a proton from the starting ketone or to abstract a proton (or a hydrogen atom) from the solvent when no other proton donor was present. Any protonated anion radical produced was reduced further by the addition of a second electron per molecule. Thus, the number of electrons transferred to each molecule of the *trans*-ketone **11**, a compound which lacks acidic hydrogen atoms, varied between one and two depending on the temperature and, probably, also on the rate of addition and mixing during the titration. The subsequently

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(20) The stability of solutions of sodium and *t*-butyl alcohol in liquid ammonia containing a low concentration of sodium *t*-butoxide has been noted by R. R. Dewald and R. V. Tsina, *Chem. Commun.*, 647 (1967).

(21) E. Müller, A. Rieker, K. Scheffler, and A. Moosmayer, *Angew. Chem. Intern. Ed. Engl.*, 5, 6 (1966).

(22) See ref 19d and (a) H. Strehlow in "The Chemistry of Non-Aqueous Solvents," Vol. 1, J. J. Lagowskii, Ed., Academic Press, New York, N. Y., 1966, pp 129–172; (b) J. J. Lagowskii and G.A. Moczygema, *ibid.*, Vol. 2, 1967, pp 340–342; (c) C. A. Kraus, *J. Amer. Chem. Soc.*, 36, 864 (1914); J. L. Dye, G. E. Smith, and R. F. Sankuer, *ibid.*, 82, 4803 (1960).

(23) See Table II, footnote *c*.

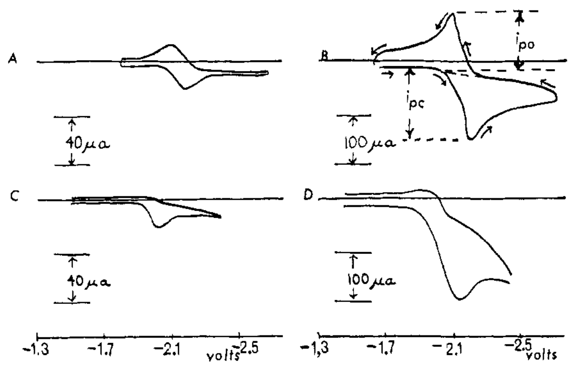


Figure 2. Typical curves from cyclic voltammetry of *trans-t*-BuCH=CHCOBu-*t* with various ketone concentrations, scan rates, and solvents: A, 1.0 × 10^{-3} *M*, 0.28 V/sec, DMF; B, 1.0 × 10^{-3} *M*, 28 V/sec, DMF; C, 0.9 × 10^{-3} *M*, 0.31 V/sec, 5.5 *M* H_2O in DMF, pH ~13; D, 0.9 × 10^{-3} *M*, 30 V/sec, 5.5 *M* H_3O in DMF, pH ~13. In these curves currents below the zero lines are cathodic. The electrode area is 5 × 10^{-2} cm^2.

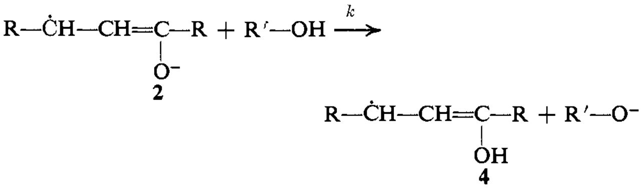
described preparative experiments provide additional evidence for this hypothesis.

The epr spectra of solutions obtained by treating a Na–HMP–THF mixture with 1 equiv or less of the *trans*-ketone **11** exhibited either no signal or (with excess Na) only the singlet observed for solutions of Na in HMP–THF mixtures. These observations made at −35° suggest that at least in the absence of excess Na the paramagnetic radical anion **16** and/or **17** does not survive in these solutions. The subsequently discussed effect of metal cations on the lifetime of the radical anion **16** is consistent with this idea.

Measurement of Anion Radical Half-Lives by Cyclic Voltammetry. The reduction of solutions of the ketone **11** in DMF or HMP containing *n*-Pr_4NClO_4 at a mercury-coated spherical Pt electrode was examined by cyclic voltammetry employing a single triangular potential sweep.[24] Under anhydrous conditions the half-life of the intermediate anion radical **16** exceeded 10 sec as illustrated in Figure 2 by the complete reoxidation of the intermediate during the anodic portion of the voltage sweep. The following criteria[24] for a reversible electron transfer were observed: (1) the value i_{pa}/i_{pc} (the ratio of the anodic peak current to the cathodic peak current) remained constant at sweep rates (ν in volts/second) which varied from log ν = −1 to log ν = 2; (2) a plot of E_{pc} (the value of the potential at the peak cathodic current) *vs.* log ν gave the form expected[24] for a reversible electron transfer; (3) a plot of $i_{pc}/\sqrt{\nu}$ *vs.* log ν has a slope of zero.

When the same measurements were repeated with solutions which contained water, aqueous buffers (pH 9 and 13), alcohols, or low concentrations of Li^+ cation the lifetime of the anion radical was markedly reduced. The plots of E_{pc} *vs.* log ν and of $i_{pc}/\sqrt{\nu}$ *vs.* log ν now exhibited the behavior expected[24] of reactions in which a reversible electron transfer is followed by an irreversible chemical step.

The half-life of the anion radical **16** could be estimated from the values of i_{pc} (related to the concentration, C_0, of anion radical initially produced in the liquid layer surrounding the electrode) and i_{pa} (related to the concentration, C_t, of radical anion remaining in the layer surrounding the electrode at the time of reoxidation). The scan rate, ν, was varied until i_{pa}/i_{pc} = 0.50. For electrochemical processes in which a reversible charge transfer (*e.g.*, **1** $\rightleftharpoons$ **2**) is followed by an irreversible chemical step (*e.g.*, **2** → **4**), Nicholson and Shain[24] have calculated that when $i_{pa}/_{pc}$ = 0.50



$$\underset{\mathbf{2}}{R\text{—}\dot{C}H\text{—}CH\text{=}\underset{O^-}{C}\text{—}R} + R'\text{—}OH \xrightarrow{k} \underset{\mathbf{4}}{R\text{—}\dot{C}H\text{—}CH\text{=}\underset{OH}{C}\text{—}R} + R'\text{—}O^-$$

the rate, *k*, of the chemical step which is first order in the anion radical **2** is given by the relation $k = 0.982/\tau$. In this relationship τ is the time in seconds between the half-wave potential, $E_{1/2}$ for reduction of the ketone and the switching potential, E_λ, the point at which the direction of the voltage scan is reversed.[24] In other words, $\tau = (E_{1/2} - E_\lambda)/\nu$. Assuming the chemical reaction (*e.g.*, **2** → **4**) to be first order in the radical ion **2**, the half-life, $t_{1/2}$, of the radical ion is $t_{1/2} = 0.693\tau/0.982$ or 0.706τ. Utilizing these relationships the variations in the half-life of the radical ion **16** with changes in reaction conditions and concentrations were calculated and are summarized in Table III.

We have also utilized an alternative procedure for estimating anion radical half-lives which is conceptually simpler but has not been justified by theoretical treatment. In this alternative treatment, the scan rate, ν, is again varied until i_{pa}/i_{pc} = 0.50. The elapsed time, *t*, between the appearance of the cathodic peak, E_{pc}, and the anodic peak, E_{pa} was readily measured from the relationship $t = \Delta V/\nu$ where ΔV is the total magnitude (irrespective of sign) of potential change between the cathodic and anodic peaks [*i.e.*, $\Delta V = (E_{pc} - E_\lambda) + (E_{pa} - E_\lambda)$]. If the relationship $i_{pa}/_{pc} = C_t/C_0$ is approximately correct under the conditions of our measurements (where $E_{1/2} - E_\lambda$ = 250–400 mV) for the layer of solution surrounding the electrode, then *t* is the time required for the initial concentration, C_0, of anion radical to decay to one-half its initial value. The results of these calculations are also summarized in Table III. Although the half-life values obtained by the two procedures are of the same order of magnitude, the values calculated by Nicholson and Shain's procedure are invariably shorter by a factor of 2–4.

Since the half-life values calculated by either procedure for the anion radical **16** in DMF–H_2O mixtures are independent of the concentration of the starting ketone **11**, our assumption that the rate of disappearance is first order in the radical anion **16** is justified. Our data also suggest that the disappearance of the radical anion is first order in alcohols added as proton donors and support a rate-limiting proton transfer step to form an allylic radical (*i.e.*, **2** → **4**).

Although solutions of the radical anion **16** are relatively stable in the presence of *n*-Pr_4N^+ cation and low concentrations of Na^+ cation, the effect of low concentrations (10^{-2}–10^{-3} *M*) of Li^+ is striking.[25] Evidently in the solvents of intermediate polarity (dielectric constant 30–40) being used, only the small

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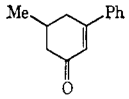
[24] R. S. Nicholson and I. Shain, *Anal. Chem.*, 36, 706 (1964); 37, 178 (1965).

[25] The ability of Li^+ cation to intercept the radical anion derived from the electrolytic reduction of *p*-benzoquinone has been noted recently by B. R. Eggins, *Chem. Commun.*, 1267 (1969).

Table III. Half-Life Values for Anion Radicals from Representative α,β-Unsaturated Ketones

Ketone	Concn, M	Solvent	Additive	Log ν, V/sec	ΔV, V	$-E_{1/2}$, V *vs.* sce	$-E_\lambda$, V *vs.* sce	Half-life, sec	
								$t_{1/2} = \Delta V/\nu$	$t_{1/2} = 0.706\tau$
trans-*t*-BuCH=CHCOBu-*t*	1.0×10^{-3}	DMF						>10	
	0.9×10^{-3}	DMF	5.5 M H_2O (pH ~13)	2.55	0.95	2.00[a]	2.45	3×10^{-3}	0.9×10^{-3}
	0.9×10^{-3}	DMF	5.5 M H_2O (pH ~9)					$<10^{-3}$	
	1.0×10^{-3}	DMF	0.5 M H_2O	0.25	0.75	2.22[a]	2.60	0.4	0.2
	1.0×10^{-3}	DMF	1.2 M H_2O					$<10^{-3}$	
	1.1×10^{-3}	DMF	0.5 M *t*-BuOH	0.65	0.75	2.22[a]	2.52	0.2[b]	0.05[b]
	1.3×10^{-3}	DMF	0.5 M *i*-PrOH	0.25	0.75	2.22[a]	2.50	0.4	0.1
	1.1×10^{-3}	DMF	0.03 M CF_3CH_2OH					$<10^{-3}$	
	2.2×10^{-3}	HMP						>50	
	4.8×10^{-3}	HMP	2.2 M H_2O	0.15	0.75	2.14[c]	2.60	0.5	0.2
	$1.2\text{–}4.8 \times 10^{-3}$	HMP	1.1 M H_2O	−0.70–0.80	0.75	2.14[c]	2.60	4–6[d]	1.6–2.0[d]
	2.2×10^{-3}	HMP	0.63 M H_2O					>20	
	2.0×10^{-3}	HMP	1.1×10^{-3} M $LiClO_4$	−1.10	0.75	2.15[c]	2.66	9	5
	2.0×10^{-3}	HMP	2.2×10^{-3} M $LiClO_4$					<0.7	
	2.0×10^{-3}	HMP	4.5×10^{-3} M $NaClO_4$					>50	
cis-*t*-BuCH=CHCOBu-*t*	1.7×10^{-3}	DMF						>10	
trans-MeCH=CHCOMe	2.0×10^{-3}	DMF		2.60	1.11			*Ca.* 3×10^{-3}	
trans-PhCH=CHCOBu-*t*	2.2×10^{-3}	DMF		0.00	0.78			*Ca.* 0.5	
	2.2×10^{-3}	DMF	5.5 M H_2O (pH ~13)	1.30	0.63			*Ca.* 2×10^{-2}	
$Me_2C{=}CHCOMe$	1.8×10^{-3}	DMF		1.40	1.0			*Ca.* 4×10^{-2}	
trans-PhCH=CHCOPh	2.0×10^{-3}	DMF	5.5 M H_2O (pH ~13)	1.22	0.60			*Ca.* 4×10^{-2}	
	2.0×10^{-3}	DMF	5.5 M H_2O (pH ~9)	2.49	0.40			*Ca.* 1×10^{-3}	
	1.0×10^{-3}	DMF						>10	

[a] $E_{1/2}$ value obtained from Table I. [b] Over the concentration range 0.2–0.8 M *t*-BuOH; the reciprocal of the half-life is directly proportional to the *t*-BuOH concentration. [c] $E_{1/2}$ value estimated from the relationship $(E_{pa} + E_{pc})/2$ with cyclic scan data obtained at rapid scan rates. [d] Within the limits of error in our measurements, the half-life was independent of the concentration of the starting enone.

Li^+ cation is able to rapidly exchange its solvent ligands with the radical anion. The resultant ion pairing, which will reduce the electrostatic repulsion between radical anions, will favor dimerization[18f] just as protonation of the anion radical (*e.g.*, **2** → **4**) leads to rapid dimer formation. The protonated anion radicals (or anion–Li^+ ion pairs) apparently react very rapidly since successive repetitive cyclic scans failed to indicate the presence of any intermediates such as the allylic radicals **4** which would be expected to undergo reduction or oxidation at the potentials being used.

We believe that the principal reason for the unusual stability of the radical anions derived from the di-*t*-butyl enones **11** and **14** compared with other aliphatic enones (see Table III) is the absence of acidic hydrogen atoms in the starting enones **11** and **14**.[26] Most aliphatic α,β-unsaturated ketones possess acidic hydrogen atoms at the α′-carbon and/or the γ-carbon atom. Consequently, if no relatively acidic proton donor is added during the reduction of these substances, a portion of the starting material can function as a proton donor and be converted to an enolate anion which is relatively resistant to further reduction. We believe this to be the primary reason why it is necessary to add alcohols to the reaction mixture in order to obtain high yields of reduced products in reductions of aliphatic enones with $Li\text{–}NH_3$ solutions.[4k,n]

Preparative Electrolysis and Coulometry. Small-scale controlled-potential electrolyses were performed in a three-compartment cell with a stirred mercury pool cathode.[27] A gas coulometer[28] in series with the cell permitted measurement of the total current passed through the cell. When the catholyte consisted of a solution of the *trans*-ketone **11** and $n\text{-}Pr_4NClO_4$ in anhydrous DMF, a relatively stable solution of the

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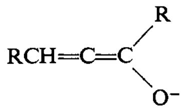
[26] We have found no evidence to indicate the α,β-unsaturated ketones (1) react with even relatively strong bases such as $Ph_3C^-Li^+$ to form vinyl enolate anions



$$RCH{=}C{=}C\begin{matrix}R\\O^-\end{matrix}$$

See (a) B. A. Tefertiller, Ph.D. Dissertation, Massachusetts Institute of Technology, Cambridge, Mass., 1965, pp 111–113, 136–139; (b) H. O. House and W. F. Fischer, Jr., *J. Org. Chem.*, **34**, 3615 (1969); (c) for other discussion see B. W. Rockett, T. M. Harris, and C. R. Hauser, *J. Amer. Chem. Soc.*, **85**, 3491 (1963).

[27] L. Meites, "Technique of Organic Chemistry," Vol. 1, part 4, A. Weissberger, Ed., Interscience Publishers, Inc., New York, N. Y., 1960, pp 3281–3333.

[28] J. A. Page and J. J. Lingane, *Anal. Chim. Acta*, **16**, 175 (1957).

anion radical **16** was produced as the electrolysis proceeded and the catholyte became a yellow brown color. If the current was interrupted the measured potential between the cathode and the reference electrode was 2.22 V (*vs.* sce). The absorption spectra of the catholyte solution exhibited one maximum in the visible at 435 mμ ($\epsilon > 400$) with end absorption at 350 mμ. The epr spectra of these colored solutions are identical with the spectra described previously (Figure 1).

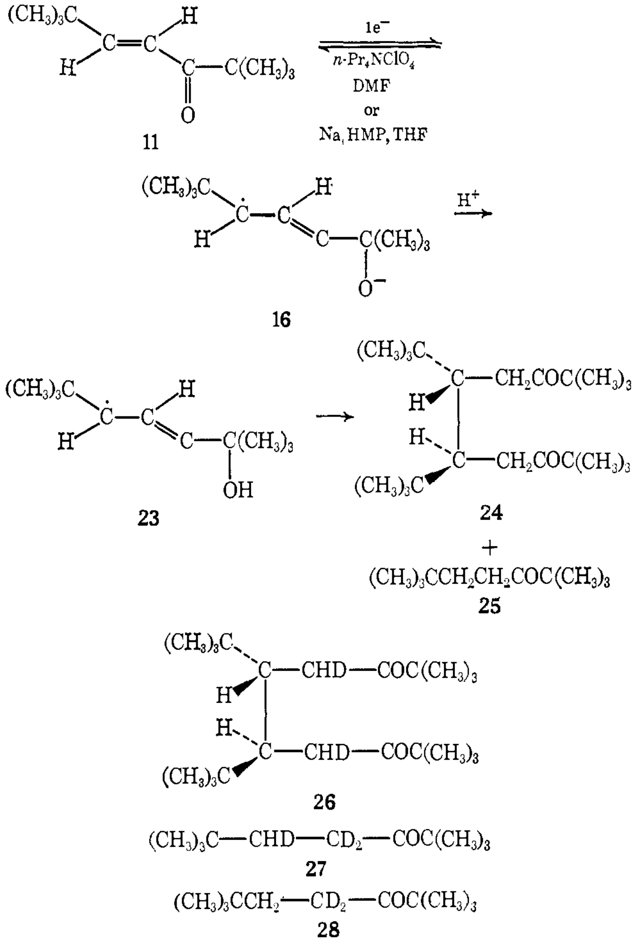
The color, epr absorption, and potential difference, attributable to the radical anion **16**, are immediately discharged by the addition of either oxygen or a proton donor such as water. With rigorous attention to maintaining oxygen-free, anhydrous conditions, the epr signal and the color of the anion radical **16** could be maintained for periods of 1 hr or more. As might be expected from our study of half-lives, the formation of a stable radical anion was not observed when the ketone **11** was electrolyzed in HMP solution containing $LiClO_4$ as the supporting electrolyte. The products of this electrolysis were the dihydrodimer **24** (45% yield) and the monoketone **25** (10% yield).

After a solution of the radical anion **16** had been prepared by electrolysis of the *trans*-ketone **11** an equimolar quantity of the β-deuterio ketone **13** was added. The epr spectrum of the resulting solution was a composite of the spectra (Figure 1, curves A and B) for the nondeuterated and β-deuterio anion radicals demonstrating the occurrence of relatively rapid electron exchange between the anion radical **16** and the starting enone **11** or **13**.

The rate of decay of the anion radical, measured by the absorption peak at 435 mμ and the epr signal was followed with time at 22.5 or 27°. Since this decay rate behaved as a first-order process ($k = 4 \times 10^{-4}$–10×10^{-4} sec^{-1} in various measurements), we believe that the radical anion **16** is being lost by reaction with the solvent, starting ketone, or some impurity in the reaction system. Since the observed decay rate was essentially the same in solutions containing either 0.1 *M* or 0.2 *M* n-Pr_4NClO_4, reaction of the anion radical with the supporting electrolyte appears not to be a major reaction path. Gas chromatographic analysis of the product remaining after decay of the radical anion **16** revealed the major product to be the subsequently described racemic dihydrodimer **24** (30% yield, Scheme III). Smaller amounts of the monoketone **25** (15% yield) were also present. These observations combined with subsequently described experiments suggest that the principal reaction of the anion radical **16** is proton abstraction from some species in the reaction solution to form a protonated intermediate **23** which rapidly dimerizes or disproportionates.

When the preparative electrolysis was performed with a catholyte containing the ketone **11** and n-Pr_4NClO_4 in a mixture of DMF and an aqueous buffer (pH 9 or 13), the same dihydrodimer **24** was isolated in 55–60% yield and current ceased when 1.00–1.06 Faraday/mol of ketone **11** had passed through the cell. The monoketone **25** (5–10% yield) was also found. When the reaction was performed with D_2O rather than H_2O in the catholyte, the racemic dihydrodimer isolated contained 12% d_1, 62% d_2, 22% d_3, and 4% d_4 species: the mass spectrum of the product indicates structure **26** to be the principal dideuterated species.

Scheme III



Preparative Reductions with Sodium Metal. Reduction of the ketone **11** with Na–HMP–THF mixtures under various conditions (Table IV) yielded mixtures of the monomeric (**25**) and dimeric (**24**) reduction products after the crude product had been oxidized with H_2CrO_4 to reconvert any alcohols present to ketones. Generally high yields of the monomeric product **25** were obtained in all reactions where a proton donor (*e.g.*, *t*-BuOH) was present while the ketone **11** was being reduced. When the reduction was performed in the presence of *t*-BuOD and the crude product was subjected to base-catalyzed hydrogen–deuterium exchange, the major product was the trideuterio ketone **27**. Since the conditions used for the hydrogen–deuterium exchange converted the ketone **25** to the dideuterio ketone **28**, we conclude that the bulk of the hydrogen (or deuterium) added to the β-carbon was derived from a proton donor (*i.e.*, *t*-BuOH or *t*-BuOD) and not a hydrogen atom donor. Further justification for this conclusion came from reduction of the ketone **11** in the presence of $(CH_3)_2CDOH$, a good deuterium atom donor.[29] The monomeric reaction product after subsequent base-catalyzed H–D exchange was the dideuterio ketone **28**; a comparable result was obtained

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[29] (a) P. A. Leermakers, P. C. Warren, and G. F. Vesley, *J. Amer. Chem. Soc.*, **86**, 1768 (1964); (b) S. G. Cohen and R. J. Baumgarten, *ibid.*, 87, 2996 (1965); **89**, 3471 (1967); (c) S. G. Cohen and H. M. Chao, *ibid.*, **90**, 165 (1968); (d) S. G. Cohen, N. Stein, and H. M. Chao, *ibid.*, **90**, 521 (1968).

Table IV. Reduction of the Ketones **11** and **14** with Sodium

			Product yields, % (product compositions, %)			
Reactants and solvents	Temp, °C	Reaction time after mixing	*trans*-Ketone **11**	*cis*-Ketone **14**	Dihydromonomer **25**	Dihydrodimer **24** or **30**
11 + excess solid Na in THF	0	2 hr			<2	98
11 + excess solid Na + *t*-BuOH (6.0 equiv) in THF	0	2 hr			73	27
Na (1.0 equiv) soln in HMP–THF (2:1) added within 2 sec to **11** in HMP–THF (3:2)	−10	2 sec	33		33[a]	34
	25	5 sec	16		28	53
Excess Na (*ca.* 3–5 equiv) soln in HMP–THF (2:1) added slowly over 1 hr to **11** in HMP–THF (2:1)	0	30 min			83	14
Na (1.9[b] or 6.0 equiv) soln in HMP–THF (3:2) added within 60 sec to **11** in HMP–THF (3:2)[b]	−33	60 sec	0–4		18–25	70
Na (6.7 equiv) soln in HMP–THF (3:2) added within 5 sec to **11** in HMP–THF; after 60 sec, *t*-BuOH (3.0 equiv) was added	−33	10 min			28	64
Na (4.6 equiv) soln in HMP–THF (3:2) added within 60 sec to **11** + *t*-BuOH (3 equiv) in HMP–THF (3:2)[b]	−33	60 sec			68	28
Na (1.0 equiv) soln in HMP–THF (2:1) added within 2 sec to **14** in HMP–THF (3:2)	−10	2 sec	(27)	(2)	(24)[c]	(47)
11 in THF added within 3 sec to Na (1.0 equiv) soln in HMP–THF (1:4)	−78	5 sec	(11)[d]	(1)	(5)	(83)
11 in HMP–THF (2:1) added within 60 sec to Na (1.3–1.8 equiv) soln in HMP–THF (2:1)	−33	10 sec	8		8	75
	25	10 sec	5		55	35
11 in HMP–THF (2:1) added slowly over 2 hr to Na (solid + soln) in HMP–THF (2:1)	25	5 min			92	8
14 in THF added within 3 sec to Na (1.0 equiv) soln in HMP–THF (1:4)	−78	2 sec	16[e]	10	21	38
11 in HMP added slowly over 1.5 hr to excess Na (solid + soln) + *t*-BuOH (3.0 equiv) in HMP	0	15 min			82	16
11 in THF added within 60 sec to Na (3.2 equiv) soln + Me_2CDOH (5.0 equiv) in HMP–THF (1:5)	−78	5 min	3		78[f]	21

[a] After quenching with D_2O and H–D exchange, the material contained 3% d_0, 25% d_1, and 72% d_2 species. [b] In these reactions the Na solution was added until a blue color was obtained in the reaction solution indicative of the presence of a slight excess of Na. [c] After quenching with D_2O and H–D exchange, the material contained 1% d_0, 11% d_1, and 88% d_2 species. [d] After quenching with D_2O, the material contained <1% deuterated species. [e] The material recovered after quenching with D_2O contained 65% d_0 and 35% d_1 species. From the presence of ir absorption at 1130 cm^{-1} and the pattern of nmr absorption at δ 6.87, we conclude that the d_1 species is primarily the α-deuterio ketone **8**. [f] After H–D exchange this product contained 93% d_2 and 7% d_1 species.

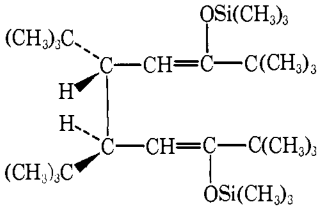
from reduction of the ketone **11** with Li–NH_3(liq) containing $(CH_3)_2CDOH$. These results taken with the earlier reported[41] reduction of α,β-unsaturated ketones with Li + *n*-$PrND_2$ to form β-deuterio ketones constitute a compelling argument for the notion that the hydrogen added at the β-carbon is normally derived from a proton donor rather than a hydrogen atom donor.

A series of reductions (Table IV) of the ketone **11** were performed by reaction of the ketone with Na–HMP–THF mixtures followed by the addition of a proton source such as H_2O (or D_2O), MeOH, or *t*-BuOH. Although the material balances were normally satisfactory in these reactions, the proportion of monomer **25** to dihydrodimer **24** in the reaction product varied substantially with changes in reaction temperature and with changes in the time or order of mixing.

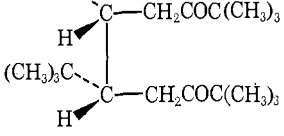
Reductions at room temperature usually yielded more monomeric product **25**; when such reaction mixtures were quenched with D_2O, the monomeric product after base-catalyzed hydrogen–deuterium exchange was the dideuterio ketone **28** which lacked deuterium at the β position. A comparable result was obtained by Normant and coworkers,[4f] who suggested that the hydrogen added to the β-carbon in these reductions was probably derived from abstraction of a hydrogen atom from the solvents. We have already cited evidence indicating that this is not the case when a proton donor is present during the reduction. Our observation that HMP can apparently serve as a proton donor for strong bases (*e.g.*, MeLi) raises the possibility that HMP can also serve as a proton donor in a reaction with a radical anion.

At relatively low temperatures (−35 to −70°) substantial yields of the dihydrodimer **24** were obtained (Table IV) when the ketone **11** was added to solutions of sodium in HMP–THF mixtures and the reaction mixtures were then quenched with MeOH. When the reaction mixtures were quenched with trimethylsilyl chloride rather than a proton donor the corresponding dienol ether **29** was produced. These results coupled with the previously described epr and half-life studies suggest that when anion radical **16** is associated with an alkali metal cation (a circumstance that would be favored by low temperatures and THF as cosolvent), the associated anion radical dimerizes rapidly even in the absence of a proton donor to form a dienolate anion which is the precursor of the bis-silyl ether **29**.

Further evidence for the existence of two geometrically isomeric anion radicals was obtained when either the *cis* (**14**) or *trans* (**11**) ketone was reduced at low temperatures and then quenched with a protic solvent. At −35° the products obtained from either ketone **11** or **14** were a mixture of the dihydrodimer **24** and the monomer **25**. Apparently at −35° the initially formed anion radicals **16** or **17** are rapidly equilibrated to form the more stable *trans*-anion radical **16** which produces the observed products **24** and **25** after protonation. However at −78° the interconversion of **16** and **17** is apparently sufficiently slow to allow the *cis*-anion radical **17** to survive for several minutes. From reductions at −78° the usual racemic dihydrodimer **24** was formed from the *trans*-ketone **11** but a new *meso*-dihydrodimer **30** was produced from the *cis*-ketone **14**



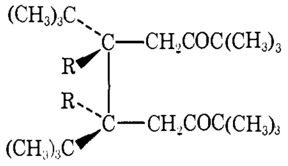
29



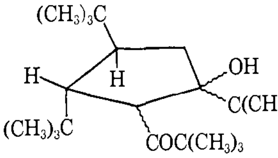
30

Reduction of either ketone **11** or **14** with a suspension of metallic sodium in THF (Table IV) yielded the racemic dihydrodimer **24** as the major or exclusive product. The same reduction procedure in the presence of a proton donor (*t*-BuOH) yielded the monomer **25** as the major reduction product.

Structure and Stereochemistry of the Dihydrodimers. The nmr spectrum of the racemic dihydrodimer **24**, mp 127–128°, exhibits two closely spaced *t*-butyl signals and a complex multiplet attributable to protons in the α and β positions. The dideuteriodimer **31**, obtained by reducing the deuterio ketone **13** with Na in THF, exhibits a simple AB pattern in the nmr with $J = 19$ Hz indicative of a symmetrical structure with coupling between nonequivalent geminal protons. Thus, only dimers bonded at the β-carbon atoms (structure **24** and its stereoisomers) need be considered. In certain of the crude reduction mixtures an unstable product thought to be one of the stereoisomers of the aldol product **32** was detected. Although our efforts to isolate a pure sample of this material resulted in its conversion to the racemic diketone **24** or other unidentified products, a comparable aldol product has been isolated in a related case.[3] The ready formation of an aldol product such as **32** is consistent with the racemic stereochemistry assigned since formation of the corresponding aldol product from the *meso*-dihydrodimer **30** would require eclipsing the adjacent *t*-butyl groups. We subjected the dihydrodimer **24** to nitric acid oxidation to obtain the previously described[30] anhydride **33** which had been shown to possess the racemic configuration by partial resolution.[30] An analogous oxidation of the dideuterio dimer **31** produced the dideuterio anhydride **34** demonstrating the absence of epimerization during the nitric acid oxidation. These results establish the structure and stereochemistry of the racemic dihydrodimer **24**.

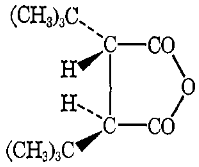


24, R = H
31, R = D

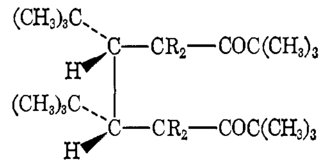


32

The second dihydrodimer **30**, mp 90–91°, has nmr and mass spectra very similar to those of the racemic isomer **24** and was shown also to arise from bonding between the β-carbon atoms of the starting enone **14** by base-catalyzed H–D exchange to form the tetradeuterio dimer **35**. Consequently, this material must possess the indicated *meso* stereochemistry.



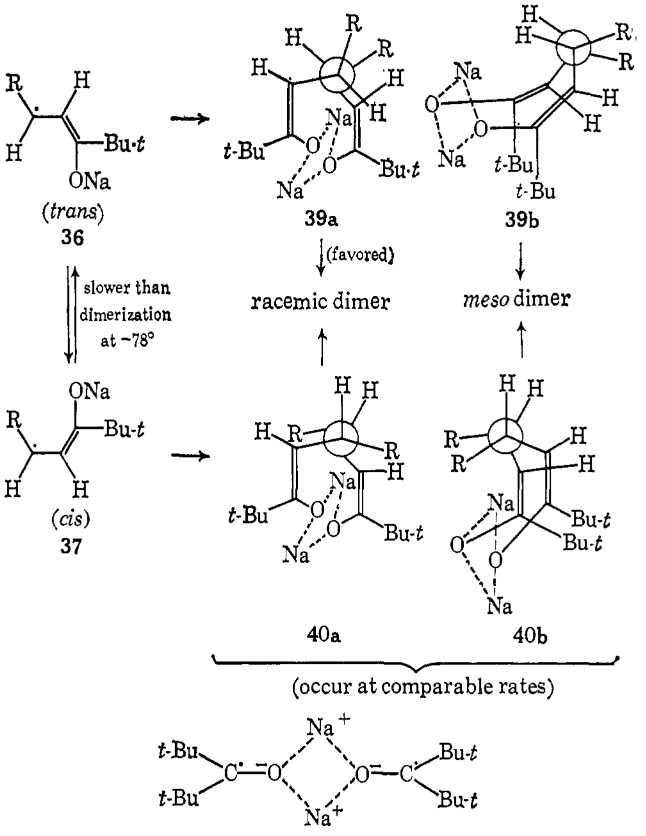
33, R = H
34, R = D



30, R = H
35, R = D

Both here and in a related study,[3] the dimerization of metal ketyls derived from enones of the type R—CH=CH—CO—Bu-*t* follows the stereochemical course illustrated in Scheme IV in which the *trans*-anion radical **36** yields practically exclusively the racemic dimer whereas the *cis*-anion radical **37** yields both stereoisomeric dimers. When these observations are considered in the light of earlier studies of Weissman and Hirota[11] showing that metal ketyls exhibit a marked tendency to exist as dimeric ion pairs such as **38**, a possible explanation for these stereochemical results is apparent. If metal ketyls bridged by alkali metal cations are considered to be the precursors to dimerization, Scheme IV illustrates the geometrical relationships (structures **39** and **40**) leading to *meso* and *racemic* dimers. It will be noted that only in structure **39a** (*trans*-anion radical → racemic dimer) is partial eclipsing of each large substituent with another large substituent avoided during the formation of a new bond between the β-carbon atoms. A structure similar to **39a** with hydrogen bonds bridging the two radicals could be written to account for the formation

Scheme IV



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(30) L. Eberson, *Acta Chem. Scand.*, 13, 40 (1959).

of a racemic dimer in the electrochemical reductions. However, the rapid interconversion of stereoisomeric anion radicals such as **16** and **17** under the conditions required for preparative electrochemical reductions has thus far prevented us from knowing whether these dimerizations in electrochemical reductions are stereospecific processes.

Discussion

Our data are consistent with the reaction path illustrated in Scheme I in which the initial radical anion **2** is formed reversibly by addition of one electron to an aliphatic enone. Presumably for reasons of electrostatic repulsion, dimerization or further electron addition to the relatively free anion radical **2** is either very slow or does not occur. However, either formation of a tight ion pair with a metal cation (*e.g.*, **3**) or protonation (*e.g.*, **4**) diminishes this electrostatic repulsion so that dimerization or further reduction can occur as rapid competitive processes. In the absence of any proton donor (*i.e.*, ROH, solvent, or a starting enone with acidic H atoms), dimerization of the ion pair **3** is favored over further reduction. This may well be a result of the previously discussed existence of these metal ketyls as dimeric ion-pair aggregates. The rates of dimerization (**4** → **6**) and reduction (**4** → **7**) appear more nearly comparable with the protonated intermediate **4**. In reductions with solutions of metals at relatively high concentrations where bimolecular encounters between the radical **4** and an electron donor are probable, the electron transfer **4** → **7** is favored. However, in processes such as electrochemical reductions or reductions at a metal surface (*e.g.*, Na + THF), where the radical **4** must diffuse to a surface for further electron transfer, dimerization (**4** → **6**) of the radical **4** becomes the probable reaction path.

Although addition of this radical **4** to another molecule of unreduced enone (**4** → **10**) clearly occurs in some cases (particularly at very high concentrations of reactive α,β-unsaturated carbonyl compounds),[40] we believe that the dimer formation which we are observing at 10^{-2}–10^{-3} M concentrations is primarily the result of dimerization of the allylic radicals (**4**). It is not clear whether the small amounts of monomeric reduction products (**9**) observed in our electrochemical reductions are best attributed to an electron transfer between two radicals (**4**) (*i.e.*, disproportionation to form **7a** and **1**) or to further reduction of a small amount of the radical **4** at the cathode. Also, the lifetimes and structures of intermediates formulated in Scheme I as enolic anions (**7a**) or enolic organometallic reagents (**7b**) are obviously open to question and further experimentation will be required to resolve these uncertainties.

Experimental Section[31]

Preparation of the *trans*-Ketone 11. A cold (0°) solution of 17.2 g (20.0 mmol) of pivaldehyde and 40 g (40.0 mmol) of pinacolone in 50 ml of Et_2O was treated with 25 ml of ethanolic 1 M NaOH and the reaction mixture was stirred for 48 hr at room temperature and then refluxed for 1 hr. After the resulting mixture had been washed with aqueous NaCl, the bulk of the solvent and unchanged pinacolone were removed by fractional distillation. Cooling a MeOH solution of the residual liquid on Dry Ice caused the *unsaturated ketone* **11** to separate. After the material had been washed with cold (−78°) MeOH and pentane, the product was obtained as 12.5 g (37%) of white needles, mp 42–43°, which exhibited a single glpc peak (Carbowax 20M). A sample of the ketone **11** collected by glpc was sublimed at atmospheric pressure to give the pure **unsaturated ketone 11**: mp 44–44.5°; ir (CCl_4) peaks of comparable intensity at 1690 (conj C=O) and 1625 cm^{-1} (conj C=C); uv (95% EtOH) 228 (ϵ 12,700) and 320 mμ (ϵ 59); uv (DMF) 322 mμ (ϵ 51); nmr (CCl_4) AB pattern with J = 15.5 Hz and estimated line positions of δ 6.20 and 6.74 (2 H, *trans*-CH=CH) and partially resolved singlets at 1.08 and 1.10 (18 H, $(CH_3)_3C$); mass spectrum, molecular ion peak at m/e 168 with abundant fragment peaks at m/e 112, 111, 57, 55, and 41.

Anal. Calcd for $C_{11}H_{20}O$: C, 78.51; H, 11.98. Found: C, 78.58; H, 11.93.

In subsequent preparations of **11** it was most convenient to form a pentane solution of pivaldehyde by reaction of *t*-BuLi with DMF followed by hydrolysis. This pentane solution was distilled and then used directly in the aldol condensation. In a typical run with 0.895 mol of *t*-BuLi, 34 g (18% overall) of the crystalline *trans*-ketone **11** was obtained.

Preparation of the *cis*-Ketone 14. In preliminary experiments, pentane solutions of the *trans*-ketone **11** were irradiated in a quartz vessel with the light (254 mμ) from the low-pressure Hg lamp of a Rayonet photochemical reactor. At photochemical equilibrium the mixture contained [glpc analysis, Carbowax 20M or 1,2,3-tris-(β-cyanoethoxy)propane (TCEP)], in order of elution, the *cis*-ketone **14** (*ca.* 40%), the *trans*-ketone **11** (*ca.* 57%), and an unidentified component [*ca.* 3%, ir (CCl_4) 1715 cm^{-1} (C=O)]. In a typical preparative run 8.7 g of *trans*-ketone **11** was dissolved in a minimum volume of pentane and the solution (total volume 12 ml) was irradiated for 72 hr and then diluted with pentane to 27 ml. This solution was cooled on Dry Ice to crystallize the bulk of the unchanged *trans*-ketone. The crystalline material which separated was redissolved in a proportional amount of pentane and the irradiation was repeated. This photolysis–low temperature crystallization sequence was performed four times to give 7.2 g of crude product which contained (glpc analysis) primarily the desired *cis*-ketone **14**. Collection from glcp (TCEP column) separated the *cis*-ketone which was distilled in a short-path still. The pure ketone **14** was collected as a colorless liquid: bp 70–80° (0.1 mm); $n^{25.8}$D 1.4354; ir (CCl_4) 1685 (conj C=O), 1630, and 1608 cm^{-1} (conj C=C); uv (95% EtOH) 228 (ϵ 6140) and 317 mμ (ϵ 40); nmr (CCl_4) AB pattern with J = 12.6 Hz and estimated line positions at δ 5.76 and 6.13 (2 H, *cis* CH=CH) with a singlet at 1.13 (18 H, $(CH_3)_3C$); mass spectrum, molecular ion peak at m/e 168 with abundant fragment peaks at m/e 112, 111, 57, 55, 43, and 41.

Anal. Calcd for $C_{11}H_{20}O$: C, 78.51; H, 11.98. Found: C, 78.30; H, 11.95.

A solution of 16.5 mg (0.098 mmol) of a mixture of ketones (79% **14** and 21% **11**), 8.0 μl of *o*-xylene (internal standard), and 10 mg (0.09 mmol) of *t*-BuOK in 500 μl of DMF was stirred under N_2 at 25–27° for 15 min and then diluted with water and extracted with pentane. Analysis by glpc (TCEP; retention times; *o*-xylene, 7.4 min; **14**, 8.7 min; **11**, 12.3 min) indicated a quantitative conversion of the *cis*-ketone **14** to the *trans*-isomer **11**. Since an appropriate control experiment demonstrated that we could easily detect the *cis*-ketone **14** extracted from a synthetic mixture containing 0.06% *cis*-ketone **14** in the mixture of ketones **11** and **14**, we conclude that the mixture obtained from our equilibration contains less than 0.1% of the *cis*-isomer **14**.

Preparation of the Monodeuterio Ketones 12 and 13. A series of seven 12-hr exchanges between 20 ml of pinacolone and 10-ml portions of refluxing D_2O each containing 0.2 g of K_2CO_3 and 0.1 g of NaCl,[32] yielded after distillation 16.6 g of deuterated pinacolone **19** which contained (mass spectral analysis) 98% d_3 species and 2% d_2 species. No signal for the methyl ketone group was detected in the

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[31] All melting points are corrected and all boiling points are uncorrected. Unless otherwise stated magnesium sulfate was employed as a drying agent. The infrared spectra were determined with a Perkin-Elmer Model 237 infrared recording spectrophotometer fitted with a grating. The ultraviolet spectra were determined with a Cary recording spectrophotometer, Model 14. The nmr spectra were determined at 60 mc with a Varian Model A-60 or Model T-60 nmr spectrometer. The chemical shift values are expressed either in cycles per second or δ values (parts per million) relative to a tetramethylsilane internal standard. The mass spectra were obtained with an Hitachi (Perkin-Elmer) mass spectrometer. Unless otherwise stated, all electrochemical reactions and all reactions involving strong bases, metals, or organometallic intermediates were performed under a nitrogen atmosphere.

[32] A. Streitweiser, R. H. Jagow, R. C. Fahey, and S. Susuki, *J. Amer. Chem. Soc.*, 80, 2326 (1958).

nmr spectrum of this product. Ethanol-*O-d* prepared from $Si(OEt)_4$,[33] was treated with a small portion of Na to remove unchanged silicate ester present and redistilled; no nondeuterated material was detected by nmr analysis. The previously described reaction procedure was followed with 16.55 g (160 mmol) of pinacolone-d_3 (**19**), 7.1 g (94 mmol) of pivaldehyde, 15 ml of Et_2O, 9 ml of EtOD, and 9 ml of a solution containing 9 mmol of NaOD in D_2O. After the reaction mixture had been washed with aqueous NaCl, the solvents and volatile reactants were removed to leave a crude product which contained (glpc, Carbowax 20M) a mixture of the desired ketone **12** and a second more slowly eluted unidentified component [ir (CCl_4) 3510 (OH) and 1690 cm^{-1} (C=O)]. Either heating the crude product with *p*-toluenesulfonic acid to 150° for 5 min or collection of the unsaturated ketone **12** by glpc (silicone fluid, no. 710) completed the dehydration. The unsaturated ketone **12** collected by glpc, mp 43–44°, contained (mass spectral analysis) 89% d_1 species and 11% d_0 species. In a second comparable reaction the crude reaction mixture was not washed with aqueous NaCl but was concentrated and subjected to direct glpc separation. In this case the collected unsaturated ketone **12** contained 93% d_1 species and 7% d_0 species. The spectra of the deuterated (**12**) and nondeuterated (**11**) ketones differed in the following respects: ir (CCl_4) a strong band found at 1080 cm^{-1} in **11** is located at 1130 cm^{-1} in **12** and the spectrum of **12** has absorption at 905 cm^{-1} and lacks absorption present at 985 cm^{-1} in **11**; abundant peaks at *m/e* 168, 111 ($M^+ - C_4H_9$), and 55 in the mass spectrum of **11** are found at *m/e* 169, 112, and 56 in **12**; nmr (CCl_4) **12** has a peak at δ 6.87 (1 H, t, J_{HD} = 2.2 Hz, β-vinyl CH) but lacks absorption at δ 6.20 present in the spectrum of **11**.

Pivaldehyde-*d* (**18**) was prepared by reaction of $DCON(CH_3)_2$ with *t*-BuLi in pentane solution. The $DCON(CH_3)$ was obtained by the following transformations:[34] anhydrous $(CO_2K)_2$ was treated with D_2O and $SOCl_2$ to form $(CO_2D)_2$; a THF solution of $(CO_2D)_2$ was pyrolyzed in a heated tube (400–450°)[35] to yield DCO_2D[35] which was converted to DCO_2Na; reaction of this salt with $(CH_3)_2NCOCl$ in HMP at 100° yielded $DCON(CH_3)_2$ (95% d_1 species) contaminated with 1–13% of $Me_2NCONMe_2$.[36] The **aldehyde 18** was collected as a colorless liquid: $n^{25}D$ 1.3820 (lit.[37] $n^{20}D$ 1.3790 for nondeuterated material); ir (liquid film) 2110, 2020 (C–D), and 1730 cm^{-1} (C=O). Reaction of this aldehyde **18** (5.0 g or 58 mmol) with 20 g (200 mmol) of pinacolone and 12 ml of ethanolic 1 *M* NaOH as previously described followed by short-path distillation (1 mm and 40–90°) afforded 25 g of distillate which contained (in order of elution by glpc, silicone no. UCW-98) unchanged pinacolone, the desired ketone **13**, and an unknown higher boiling component (possibly the aldol product). After collection by preparative glpc (silicone no. UCW-98), the product was recrystallized from pentane at Dry Ice temperatures to separate 1.722 g (10% based on the $DCONMe_2$) of the ketone **13** as white needles, mp 39–42°. Recollection (glpc, silicone no. 710) afforded the pure **unsaturated ketone 13**, mp 43–44°, containing (mass spectral analysis) 94% d_1 species and 6% d_0 species. The spectrum of the monodeuterated (**13**) and nondeuterated (**11**) materials differ in the following respects: ir (CCl_4) peaks at 1090 and 995 cm^{-1} in **13** rather than the peaks at 1080, 1010, and 985 cm^{-1} found in **11**; nmr (CCl_4) triplet (J_{HD} = 2.2 Hz) at δ 6.24 (1 H, α-vinyl CH) in **13** rather than the doublets (*J* = 15.5 Hz) found at δ 6.74 and 6.20 in **11**; abundant peaks in the mass spectrum of **11** at *m/e* 168, 111 ($M^+ - C_4H_9$), and 55 are found at 169, 112, and 56 in the mass spectrum of **13**.

Preparation of *t*-Butyl Alcohol-O-*d* and Isopropyl Alcohol-2-*d*. Alcohol-free *t*-BuOK was added to D_2O to yield after distillation crude *t*-BuOD. This crude alcohol was refluxed over CaH_2 for 4 hr[38] and then distilled to separate *t*-BuOD, bp 84°, estimated (nmr) to contain 98% of O-deuterated material. Following a general procedure described previously,[29] acetone was reduced with $LiAlD_4$ (99%, Stohler Isotope Chemicals) in Et_2O to give 49% of 2-propanol-2-*d*: bp 80–82°; ir (liquid film) 3340 (assoc OH), 2100, and 2170 cm^{-1} (C–D stretch); nmr (pure liquid) δ 5.02 (3 partially resolved lines, HO–CD< with J_{H-D} = 0.85 Hz) and 1.07 (s, CH_3) with no absorption evident at δ 3.95, the position of the center of a multiplet (>CH–OR) in nondeuterated *i*-PrOH. We estimate from the nmr spectrum that at least 95% of the product is deuterated at C-2.

Solutions of Sodium in Hexamethylphosphoramide (HMP).[18] Commercial HMP was purified by distillation from a solution containing Na (2.0 g/500 ml) to separate the solvent as a colorless liquid: bp 65° (0.4 mm) [lit.[18a] 68–70° (1 mm)]; nmr (pure liquid) δ 2.56 (*d*, J_{P-H} = 9 Hz). When pieces of freshly cut Na were added to this pure solvent with stirring at 25–30° under N_2, the metal dissolved slowly to produce a deep blue viscous solution. Aliquots were removed periodically, quenched in H_2O, and titrated for total base with standard aqueous HCl (phenolphthalein end point). Alternatively, aliquots of the blue solution were removed and pinacolone was added, dropwise and with stirring, until the blue color was discharged to leave a colorless solution. The titers, expressed as millimoles of HCl or pinacolone per gram of solution, increased concurrently to values of 0.3–0.5 mmol/g at which time the solutions tended to decompose within 5–15 min to give a yellow solution. This decomposition was accompanied by an increased rate of dissolution of the remaining Na with a rapid increase in the total base titer to values greater than 1 mmol/g. The pinacolone titer fell to zero as this decomposition proceeded and the blue color disappeared. Once this decomposition had begun, titration of the solution with pinacolone led not to colorless solutions, but rather to a yellow solution at the end point. The decomposition of these solutions appeared to be autocatalytic. When the blue solutions were exposed to a limited amount of O_2, the solutions took on a deep red color as noted by previous authors;[18] the red solutions initially obtained became yellow on further exposure to O_2. Addition of MeLi to the pure HMP resulted in the formation of a yellow color. When 2.0 ml of cold (0°) HMP was treated with 2 ml of an Et_2O solution containing 2.92 mmol of MeLi, the above mentioned formation of a yellow solution was accompanied by the immediate evolution of 55 ml of gas estimated to contain (glpc, Apiezon N on Al_2O_3) 69% CH_4 and 31% Et_2O. Both the glpc analyses and mass spectral analysis indicated that the evolved gas contained CH_4 and Et_2O, but not ethane or ethylene. The yield of CH_4 was approximately 50% based on the MeLi added. No obvious reaction was observed when limited amounts of HMP were added to ethereal MeLi.

The addition of THF to these Na–HMP solutions increased their stability substantially. In a typical preparation, a mixture of 10 g of freshly cut Na slices and 60 ml of HMP was stirred under N_2 for 1 min and then diluted with 30 ml of THF. The resulting mixture was stirred under N_2 for 1 min and then diluted with 30 ml of THF. The resulting mixture was stirred at 0° for 2 hr and then the solution was transferred under N_2 with a stainless steel cannula to another reaction vessel. This solution (HMP–THF, 2:1, v/v) could be cooled to 0° without freezing; dilution with an additional 10 ml of THF gave a solution (HMP–THF, 3:2, v/v) which could be cooled to −35° without freezing. When 30 ml of a solution of Na in HMP–THF (2:1, v/v) was added to 70 ml of cold (−78°) THF, a solution was obtained (HMP–THF, 1:4, v/v) which did not freeze at −78°. In certain solutions containing relatively high concentrations of Na, a fine precipitate (possible finely divided Na) was observed to separate from the blue solution at low temperatures (−33 to −78°). A 2.00-g aliquot of a solution of Na in HMP–THF (3:2, v/v, approximate density 0.98 g/ml at 0°) required 70 mg (0.70 mmol) of pinacolone to just discharge the blue color. Thus, the solution is 0.28 *M* in Na. Aliquots of these Na–HMP–THF solutions were stored at 25° for 4–6 hr without significant lowering of the Na titer. Although the blue color of these solutions was rapidly discharged by exposure to an oxygen-containing atmosphere or by the addition of H_2O or MeOH, tertiary alcohols such as *t*-BuOH or Et_3COH reacted with the solution relatively slowly. Solutions obtained by adding *t*-BuOH to Na–HMP solutions (with or without THF) retained their blue color for periods of several minutes. At temperatures of 0° or lower, the blue solutions containing *t*-BuOH were stable for periods of 1 hr or longer especially when excess undissolved Na was present in the reaction mixture.

A solution of Na (0.38 *M*) in HMP–THF (2:1, v/v) at 28° developed a potential of −2.96 V between a Pt electrode in the solution and a saturated calomel electrode (connected to the solution with a bridge of n-Pr_4NClO_4 in DMF) as measured with a high impedance electrometer (Instrumentation Laboratory, Inc., Model

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(33) D. J. Pasto and G. R. Mayer, *J. Org. Chem.*, **33**, 1257 (1968).

(34) For the detailed procedures see R. W. Giese, Ph.D. Dissertation, Massachusetts Institute of Technology, Cambridge, Mass., 1969.

(35) The procedure used was an adaption of several general procedures described previously; (a) I. R. Gragerov, A. F. Rehasheva, A. M. Taresenko, A. F. Levit, and I. R. Samchenko, *Zh. Obshch. Khim.*, **31**, 1113 (1961); (b) K. B. Wiberg and R. Stewart, *J. Amer. Chem. Soc.*, **78**, 1214 (1956); (c) R. C. Herman and V. Williams, *J. Chem. Phys.*, **8**, 447 (1940).

(36) This procedure was adapted from the description of E. Stein and O. Bayer, German Patent 875,807 (May 7, 1953); *Chem. Abstr.*, **52**, 10183 (1958).

(37) V. E. Althouse, K. Ueda, and H. S. Mosher, *J. Amer. Chem. Soc.*, **82**, 5938 (1960).

(38) The purification procedure of D. J. Cram and W. D. Nielson, *ibid.*, **83**, 2178 (1961).

165). The nmr spectra of these blue solutions of Na (*ca.* 0.1–0.2 *M*) in HMP exhibited a relatively sharp doublet comparable to that seen in the nmr spectrum of the pure solvent and the epr spectrum of Na–HMP–THF solutions exhibited a single peak (line width 0.130 G) at $g = 2.0022$.

A solution of Na in HMP–THF (2:1, v/v) with an initial pinacolone titer of 0.598 mmol/g and a final titer (1.5 hr later after epr measurement) of 0.511 mmol/g was thoroughly degassed and the epr signal of this solution was compared in intensity with the epr signal of a reference benzene solution containing a known amount of diphenylpicrylhydrazyl (8.79×10^{-3} *M*). The calculated concentration of unpaired electrons in the Na solution was 1.38×10^{-3} *M* corresponding to 0.25–0.29% of the total dissolved metal. These Na solutions, like those in pure HMP, exhibited relatively sharp nmr signals consistent with a low concentration of paramagnetic species being present.

Aliquots of the Na–HMP–THF solutions, standardized by titration with pinacolone, were titrated by adding samples of the various reactants listed in Table II until the blue color was just discharged. The titration values listed are average values from two or more titrations and are expressed as moles of reactant per gram atom of dissolved Na. A 1.00-g aliquot of a standard solution with a pinacolone titer of 0.30 mmol/g of solution was quenched in water; 0.31 mmol of aqueous HCl was required to neutralize this solution to a phenolphthalein end point. Thus, we concluded that 1 mol of pinacolone reacts with 1 g-atom of Na under the conditions of this titration.

Previously described procedures were used to prepare 4-*t*-butylcyclohexylideneacetone,[39] 3,5-dimethyl-2-cyclohexenone,[40] and *trans*-benzalpinalcone:[41] mp 42–43° (lit.[41] mp 43°); ir (CCl_4) 1685 (conj C=O) and 1615 (conj C=C); uv (95% EtOH) 222 (ϵ 10,400), 227 (ϵ 9840), and 292 mμ (ϵ 21,500); nmr (CCl_4) δ 6.7–7.7 (7 H, m, vinyl and aryl CH) and 1.15 (9 H, s, $(CH_3)_3C$); mass spectrum, molecular ion at *m/e* 188, abundant fragments at *m/e* 132, 131, 103, 77, 57, 51, and 41.

To a solution of 24.89 g (161.5 mmol) of 3-ethoxy-5-methyl-2-cyclohexenone[40] in 200 ml of Et_2O was added 150 ml of an Et_2O solution containing 174 mmol of PhLi. The resulting yellow solution was stirred at 25–30° for 10 min and then partitioned between cold dilute H_2SO_4 and Et_2O. The organic phase was washed successively with aqueous NaCl, aqueous $NaHCO_3$, and aqueous NaCl and then concentrated and distilled to separate the unsaturated ketone as 20.39 g (68%) of a colorless oil which crystallized on standing. Recrystallization from pentane at low temperature separated 18.81 g (62.6%) of **5-methyl-3-phenyl-2-cyclohexenone** as white prisms: mp 34–36°; ir (CCl_4) 1670 (conj C=O) and 1610 cm^{-1} (conj C=C); uv (95% EtOH) 221 (ϵ 9800) and 284 mμ (ϵ 19,400); nmr ($CDCl_3$) δ 6.8–7.7 (5 H, m, aryl CH), 6.25 (1 H, br s, vinyl CH), 1.7–3.0 (5 H, m, aliphatic CH), and 1.0–1.3 (3 H, m, CH_3); mass spectrum, molecular ion at *m/e* 186, abundant fragments at *m/e* 144, 116, and 115.

Anal. Calcd for $C_{13}H_{14}O$: C, 83.83; H, 7.58. Found: C, 83.90; H, 7.66.

Reduction of the *trans*-Ketone 11 to Monomeric Products. A. Catalytic Hydrogenation. A solution of 900 mg (5.36 mmol) of the ketone **11** in 5 ml of EtOH was hydrogenated at 25–30° and 1 atm over 200 mg of a 5% Pd–C catalyst. The H_2 uptake (120 ml or 1.0 equiv) was complete after 15 min and the resulting solution was filtered and concentrated. A pure sample of the **ketone 25** (glpc, Carbowax 20M) was collected as a colorless liquid: n^{25}D 1.4217; ir (liquid film) 1710 cm^{-1} (C=O); uv (95% EtOH) 285 mμ (ϵ, 33); nmr (CCl_4) δ 2.2–2.6 (2 H, m, CH_2CO), 1.2–1.6 (2 H, m, CH_2), 1.12 (9 H, s, $(CH_3)_3CCO$), and 0.90 (9 H, s, $(CH_3)_3C$); mass spectrum, molecular ion *m/e* 170, abundant fragments, *m/e* 113, 57, 43, 41, and 29.

Anal. Calcd for $C_{11}H_{22}O$: C, 77.58; H, 12.03. Found: C, 77.44; H, 12.97.

A 63-mg sample of the ketone **25** was converted to its **2,4-dinitrophenylhydrazone** which crystallized from EtOH as 81 mg (74%) of orange needles, mp 130.5–131.5° (lit.[42] mp 130–131°).

B. Lithium in Ammonia Containing a Proton Donor. To a solution of 360 mg (57.6 mg-atoms) of Li in 100 ml of liquid NH_3 (freshly distilled from Na) was added successively 5.4 ml (58 mmol) of *t*-BuOH and 3.212 g (19.2 mmol) of the unsaturated ketone **11** in 5 ml of THF. After the mixture had been stirred for 2 hr, the excess metal was destroyed by addition of H_2O. The NH_3 was allowed to evaporate and the residue was partitioned between water and Et_2O. The material remaining after concentration of the Et_2O phase was dissolved in cold (0°) acetone and treated with excess 8 *N* aqueous H_2CrO_4[43] to reoxidize any secondary alcohol products present. After the resulting solution had been stirred at 0° for 5 min isopropyl alcohol was added to destroy the excess oxidant and the resulting mixture was partitioned between water and Et_2O. The organic phase was washed with aqueous $NaHCO_3$, dried, and concentrated to leave the crude product as a yellow oil which contained (glpc, silicone SE-52) the reduced ketone **25** (96% of the mixture) and the dimer **24** (4% of the mixture). Distillation in a short-path still (45 mm and 84–95°) separated 2.64 g (81%) of the saturated ketone **25** as a colorless liquid, n^{23}D 1.4229, identified with the previously described sample by comparison of ir spectra.

A sample of the saturated ketone **25** was subjected to repeated base-catalyzed H–D exchange on a glpc column.[44] The collected product, the **dideuterio ketone 28**, contained (mass spectral analysis) 96% d_2 species and 4% d_1 species. The nmr spectrum (CCl_4) of this ketone **28** differs from the spectrum of the nondeuterated ketone **25** in lacking absorption in the region δ 2.2–2.6 (α-CH_2) and in exhibiting a broad singlet at δ 1.41 (2 H, β-CH_2) rather than a complex multiplet.

The reduction was repeated by treating a cold (−78°) blue solution of 168 mg (24.2 mg-atom) of Li in 30 ml of liquid NH_3 successively with 1.10 g (18.1 mmol) of cold (−78°) Me_2CDOH and 1.027 g (6.11 mmole) of the ketone **11**. After the resulting blue solution had been stirred for 10 min, the excess metal was consumed by the addition of H_2O and the crude product was oxidized with H_2CrO_4 in cold (0°) acetone and subjected to the usual isolation procedure. An aliquot of the crude product (1.557 g of yellow liquid) was mixed with a weighed portion of internal standard (*p*-dibromobenzene) and analyzed by glpc (silicone SE-52 and TCEP columns). The calculated yields were 57% of **25** and 41% of the starting ketone **11**. A collected (glpc, TCEP column) sample of the saturated ketone **25** was subjected to base-catalyzed H–D exchange on a glpc column;[44] the resulting material contained (mass spectral analysis) 92% d_2 and 8% d_1 and was thus the dideuterated ketone **28** and not **27**.

C. Sodium in HMP Containing a Proton Donor. A mixture of 30 ml of HMP, 5.35 ml (57 mmol) of *t*-BuOH, and 3.0 g (130 mg-atoms) of Na was stirred at 0° for 1 hr at which time a thick, blue mixture resulted. To this mixture was added, dropwise and with stirring over 1.5 hr, a solution of 3.202 g (19 mmol) of the ketone **11** in 10 ml of HMP. A blue color was maintained in the reaction mixture throughout this addition. After the addition was complete, the mixture was stirred for an additional 15 min and then MeOH was added to discharge the blue color and the reaction mixture was partitioned between H_2O and pentane. The organic phase was washed with aqueous NaCl, concentrated, and treated with 8 *N* aqueous H_2CrO_4 in acetone in the usual way. The resulting neutral product (2.91 g of yellow oil) contained (glpc, silicone SE-52) the saturated ketone **25** (91% of the mixture) and the dimer **24** (9% of the mixture). Distillation in a short-path still (50 mm and 90–95°) separated 2.32 g (73%) of the monomeric reduction product **25** identified with the previously described sample by comparison of ir spectra.

A comparable reduction was performed with 951 mg (5.66 mmol) of the ketone **11**, 1.5 g (65 mg-atoms) of Na, 40 ml of HMP, 20 ml of THF, and 3.0 ml (32 mmol) of *t*-BuOD. After the reaction had been quenched with methanol, washed with water, and oxidized with H_2CrO_4, the neutral product was distilled to separate the crude saturated ketone **25**. This sample was subjected to repeated base-catalyzed H–D exchange on a glpc column[44] until a constant deuterium content was obtained. The resulting sample contained (mass spectral analysis) 14% d_2, 85% d_3, and 1% d_4 species. The nmr spectrum (CCl_4) of the trideuterated ketone **27** differed from the spectrum of the nondeuterated ketone **25** in lacking absorption

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[40] H. O. House and W. F. Fischer, Jr., *ibid.*, **33**, 949 (1968).

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[42] P. D. Bartlett and M. Stiles, *J. Amer. Chem. Soc.*, **77**, 2806 (1955).

[43] D. C. Kleinfelter and P. von R. Schleyer, *Org. Syn.*, **42**, 79 (1962).

[44] This column was prepared from Carbowax 20M, KOD, and Chromosorb P following the general directions of M. Senn, W. J. Richter, and A. L. Burlingame, *J. Amer. Chem. Soc.*, **87**, 680 (1965). The deuterium content of the column was maintained with periodic injections of D_2O (three 100-μl samples) after which the column was allowed to equilibrate for 2 hr before use.

at δ 2.2–2.6 (α-CH_2) and in having a broad singlet at δ 1.41 (1 H, β-CH_2) rather than a multiplet in this region.

Effect of Reaction Conditions on the Products from Ketones 11 and 14. A series of small-scale reductions of the unsaturated ketone **11** with Na were performed as indicated in Table IV. In all cases the reductions were terminated by the addition of excess MeOH, H_2O, or D_2O to quench the reaction mixture. Whenever *t*-BuOH was present as a proton donor in the original reduction mixture, the crude products were oxidized with H_2CrO_4 in acetone solution before analysis. Unless otherwise noted in Table IV the crude reaction products were mixed with an internal standard (either *n*-butylbenzene or *p*-dibromobenzene) and analyzed by glpc. On one column (isothermal with TCEP column) the relative retention times were: ketone **14**, 13.5 min; *n*-butylbenzene, 14 min; ketone **25**, 17 min; ketone **11**, 23 min; *p*-dibromobenzene, 42 min; dimer **24** not eluted. On a second column (temperature programmed from 90 to 200° at 4° per min with a silicone SE-52 column) the relative retention times were: *n*-butylbenzene, 7.5 min; ketones **11** and **25** (unresolved), 8.0 min; *p*-dibromobenzene, 14 min; and dimer **24**, 32 min. The results of these reductions are summarized in Table IV. In certain cases after the reduction mixture had been quenched with D_2O, a collected sample of this saturated ketone **25** was subjected to base-catalyzed H–D exchange on a glpc column[44] and then analyzed by mass spectrometry.

Preparation of the Racemic Dimer 24. A solution of 14.33 g (85.3 mmol) of the ketone **11** in 100 ml of THF was stirred with 3.0 g (0.13 g-atom) of Na slices at 0° for 4 hr. The residual Na metal was separated, dissolved in 75 ml of MeOH, and the organic solutions were combined and then diluted with 600 ml of water.[45] The white solid which separated (14.21 g) was collected and recrystallized from MeOH to give 13.2 g (92%) of the dimer **24** as white needles: mp 127–128°; ir (CCl_4) 1710 cm^{-1} (C=O); uv (95% EtOH) 284 mμ (ε 60); uv (DMF) 285 mμ (ε 62); nmr (CCl_4) δ 1.8–2.9 (6 H, m, aliphatic CH), 1.13 (18 H, s, $C(CH_3)_3$), and 0.72 (18 H, s, $C(CH_3)_3$); mass spectrum, molecular ion at *m/e* 338, abundant fragments at *m/e* 239, 225, 183, 85, 57, 55, 41, and 29.

Anal. Calcd for $C_{22}H_{42}O_2$: C, 78.04; H, 12.50. Found: C, 78.09; H, 12.44.

In another reaction a cold (0°) solution of 1.013 g (6.01 mmol) of the unsaturated ketone **11** in 10 ml of HMP and 5 ml of THF was treated with 1.0 g (43 mg-atom) of Na slices. After the initially colorless solution had been stirred for 1 hr, it assumed a blue color. Stirring was continued for 1 hr and then the mixture was quenched with MeOH and subjected to the usual oxidation and isolation procedures. The crude dimer **24** amounted to 745 mg (74%), mp 114–124°. Recrystallization from MeOH afforded the pure **dihydrodimer 24** as colorless needles, mp 127–128° identified with the previous sample by comparison of ir spectra.

In a similar reaction, a cold (−35°) solution of 720.3 mg (4.30 mmol) of the ketone **11** in 16 ml of HMP and 10 ml of THF was treated, rapidly and with stirring, with 16 ml of a cold (0°) solution of 5.28 mg-atom of Na in HMP–THF (2:1, v/v). After the resulting cold blue solution had been stirred for 15 sec, 1.81 g (16.8 mmol) of Me_3SiCl was added and the colorless reaction mixture was diluted with 200 ml of cold aqueous $NaHCO_3$. The organic product was extracted with pentane and the extract was washed with aqueous NaCl, dried, and concentrated. The residue (1.324 g of colorless liquid which crystallized on standing) was recrystallized from EtOH at −78° to separate 666 mg (69%) of the disilyl ether **29** as colorless prisms, mp 58–61°. Recrystallization gave the pure **dienol derivative 29**: mp 63–64°; ir (CCl_4) 1645 cm^{-1} (C=C); nmr (CCl_4) δ 4.57 (2 H, d, J = 10.9 Hz, vinyl CH), 2.34 (2 H, d, J = 10.9 Hz, aliphatic CH), 1.07 (18 H, s, two $(CH_3)_3C$), 0.83 (18 H, 2, two $(CH_3)_3C$), and 0.29 (18 H, s, $(CH_3)_3Si$); mass spectrum, weak fragments at *m/e* 467, 425, 417, 369, and 353 with abundant fragments at *m/e* 241, 58, 43, and 15.

Anal. Calcd for $C_{28}H_{58}O_2Si_2$: C, 69.64; H, 12.11. Found: C, 69.42; H, 12.15.

The mother liquors remaining after crystallization of the disilyl ether **29** contained (glpc, silicone SE52) the dimer **24** (ret time, 7 min) and the disilyl ether **29** (ret time, 12 min). A solution of 83.1 mg (0.17 mmol) of the disilyl ether **29** and 4 ml of aqueous 6 *M* HCl in 20 ml of EtOH was stirred at 80° for 3 days. The organic product, separated in the usual way, amounted to 73.8 mg of the crude racemic dimer, mp 117–125°, identified by comparison of nmr spectra. Recrystallization from methanol afforded 55.6 mg (95%) of the pure racemic dimer **24**, mp 125–126°.

The foregoing reduction procedure with Na and THF was also performed on the β-deuterio-*trans*-ketone **13** to yield the racemic β,β′-dideuterio dimer **31**, mp 127–128°, which contained (mass spectral analysis) 84% d_2 species, 14% d_1 species, and 2% d_0 species. The nmr spectrum (CCl_4) of the dideuterio dimer **31** differed from the spectrum of the nondeuterated dimer **24** in exhibiting an AB pattern (J = 19 Hz) with estimated line positions of δ 2.01 and 2.57 (4 H, CH_2CO) rather than the complex multiplet in the region δ 1.8–2.9 present in the nmr spectrum of the undeuterated material.

When the same reduction procedure (Na and THF at 0°) was applied to 485 mg of the *cis*-ketone **14**, recrystallization of the crude product (453 mg) from MeOH gave 214 mg (44%) of the racemic dimer **24**, mp 126–127°, which was identified by a mixture melting point determination and comparison of ir and nmr spectra. The mother liquors from the recrystallization contained (glpc, silicone SE52) the dimer **24** and a minor, more slowly eluted component thought to be a keto alcohol. A collected (glpc) sample of the major component was identified as the racemic dimer **24** by comparison of infrared spectra.

A mixture of 10.90 g (33.2 mmol) of the racemic dimer **24** and 680 g of concentrated aqueous HNO_3 was heated to 105° with stirring for 24 hr. The resulting yellow solution was cooled, diluted with water, saturated with NaCl, and extracted with pentane. The pentane extract was dried and concentrated to leave 7.6 g of pale yellow oil which was taken up in methanol and cooled to −78°. The racemic anhydride **33** separated as 689 mg (10%) of white plates, mp 112–115°. Recrystallization from methanol gave the pure **anhydride 33**: mp 114–115° (lit.[34] 114–115°); ir (CCl_4) 1860 and 1785 cm^{-1} (C=O of a five-membered cyclic anhydride); nmr ($CDCl_3$) δ 2.62 (2 H, s, CH), and 1.07 (18 H, s, two $(CH_3)_3C$); mass spectrum, abundant fragments at *m/e* 156, 125, 100, 83, 70, 57, 41, and 29.

This oxidation was repeated for 2 hr at 80° with 60.3 mg of the racemic dideuterio dimer **31** and 5 ml of concentrated aqueous HNO_3. The crude organic product was extracted into pentane and the glpc peak (silicone 710 column) corresponding to the racemic anhydride **33** was collected. The mass spectrum of this sample exhibits abundant fragment peaks at *m/e* 102, 127, and 158 with intensities indicating that at least 80% of the racemic anhydride is the dideuterated material **34**.

Preparation of the *meso*-Dimer 30. To 300 ml of cold (−78°) THF was added a cold (0°) solution of 37.8 mg-atom of Na in 130 ml of HMP–THF (2:1, v/v). The resulting blue solution was stirred at −78° for 5 min and then a cold (−78°) solution of 4.889 g (29.1 mmol) of unsaturated ketones (glpc analysis, 80% **14** and 20% **11**) in 10 ml of THF was added. The resulting blue solution was stirred for 2 min at −78° and then quenched in 1.5 l. of H_2O. After this pentane extract of the reaction mixture had been washed with aqueous NaCl, dried, and concentrated, fractional crystallization of the residue (6.73 g of yellow liquid) from MeOH at −78° separated 2.27 g (46%) of a mixture of dimers **24** and **30** as white crystals, mp 80–104°. The mixture was estimated (nmr analysis) to contain 64% of the *meso*-isomer **30** and 36% of the racemic-isomer **24**. (From a comparable reduction of the pure *cis*-ketone **14**, the mixture contained 75% *meso* (**30**) and 25% racemic (**24**) material.) A series of fractional crystallizations from MeOH separated 720 mg of the previously described racemic-dimer **24** and 900 mg of the ***meso*-dimer 30** as colorless prisms: mp 90–91°; ir (CCl_4) 1705 cm^{-1} (C=O) nmr (CCl_4) δ 1.7–3.0 (6 H, m, $CHCH_2CO$ groups), 1.15 (18 H, s, $(CH_3)_3C$), and 0.83 (18 H, s, $(CH_3)_3C$); mass spectrum, molecular ion at *m/e* 338, abundant fragments at *m/e* 239, 85, 57, 41, and 29. The column (silicone SE-52) used in our glpc analysis did not resolve the two dimers **24** and **30**.

Anal. Calcd for $C_{22}H_{42}O_2$: C, 78.04; H, 12.50. Found: C, 77.94; H, 12.55.

A solution of 102.9 mg (0.304 mmol) of the *meso*-dimer **30**, NaOD (from 50 mg or 2.18 mg-atom of Na), and 10 ml of D_2O in 20 ml of $(CH_3OCH_2CH_2)_2O$ was refluxed for 5 days and then partitioned between aqueous NaCl and pentane. The organic solution was dried, concentrated, diluted with MeOH, and cooled to −78° to separate the tetradeuterio derivative **35** of the *meso* diketone as

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(45) In experiments where the reaction mixture was separated from the Na and not mixed with NaOMe before the addition of water, the crude product contained (glpc, Carbowax 20M) the dimer **24** and two more rapidly eluted components believed to be stereoisomers of the aldol product **32**. Fractional crystallization from MeOH separated a partially purified sample of this aldol: mp 105–120°; ir (CCl_4) 3600, 3580, 3500 (OH), 1710 (C=O), 1705 (sh, C=O), and 1665 cm^{-1} (H-bonded C=O). Our attempts to obtain a single pure substance from the mixture were not successful. Apparently the addition of NaOMe in MeOH facilitates the conversion of the aldol product **32** to the diketone **24**.

Table V. Cell Resistance Values

Cathode	Electrolyte	Resistance, ohms Anode–cathode	Resistance, ohms Reference–cathode
Dropping Hg electrode	0.1 *M* *n*-Pr_4NClO_4 in DMF	450	300
	0.1 *M* *n*-Pr_4NClO_4 in DMF–H_2O (9:1)	620	420
Hg coated Pt sphere	0.5 *M* *n*-Pr_4NClO_4 in DMF	85	50
	0.4 *M* *n*-Pr_4ClO_4 in DMF–H_2O (9:1)	150	100

white prisms: mp 90–91°, which contained (mass spectral analysis), *ca.* 95% d_4 and *ca.* 5% d_3 species; ir (CCl_4) 1705 cm^{-1} (C═O); nmr (CCl_4) δ 2.13 (2 H, br s, CH β to C═O), 1.15 (18 H, s, $(CH_3)_3C$), and 0.83 (18 H, s, $(CH_3)_3C$).

Polarographic Measurements. A. Solvents and Electrolytes. HMP was purified as described in a previous section and DMF (Fisher reagent grade) was purified by distillation from P_2O_5 through a 15-cm Vigreux column.[46] A mixture of 500 g of aqueous 10% *n*-Pr_4NOH and 250 g of ice was neutralized and made slightly acidic with aqueous 71% $HClO_4$. The crude *n*-Pr_4NClO_4 which separated (80.4 g) was recrystallized from either H_2O or acetone-H_2O to give 64.2 g of the pure salt as fine white needles which were dried under reduced pressure, mp 238.5–239.5° without decomposition (lit.[7a] mp 237–239°). A comparable procedure was used for *n*-Bu_4NClO_4 which separated from aqueous acetone as fine white crystals, mp 212.5–213° (lit. mp 207–209°,[47a] 213.3–213.6°[47b]). Acetonitrile was distilled successively from NaH and from P_2O_5 as previously recommended.[48] Tetraethylammonium iodide, prepared from Et_3N and EtI, was recrystallized from H_2O-EtOH as white needles, mp >220°. Nitrogen (prepurified grade) was purified by passing it at a rate of 80 ml/min or less through two successive columns (each 4 × 30 cm), the first packed with molecular seives, No. 5A, to remove H_2O and the second packed with activated BTS catalyst[49] to remove O_2. Unless otherwise stated *n*-Pr_4NClO_4 was used as the supporting electrolyte at one of the following concentrations: 0.5 *M* for anhydrous DMF; 0.1 *M* for anhydrous HMP; 0.1 *M* for anhydrous MeCN, and 0.4 *M* for DMF-H_2O (9:1, w/w) mixtures. The DMF-H_2O (9:1, w/w) mixtures were prepared from 90 g of DMF and 10 ml of aqueous 10% (0.5 *M*) *n*-Pr_4NOH. Titration of this solution with aqueous 0.1 *M* HCl to a bromocresol purple end point indicated the solution to be 0.045 *M* in hydroxide ion; this solution is subsequently described as having a pH ~13. Aliquots (20 ml or 0.90 mmol of OH^-) of this solution were mixed with 110 mg (1.80 mmol) of H_3BO_3 to give a borate buffer solution subsequently described as having a pH ~9. When portions of this solution were measured with an Ingold high-alkaline combination glass electrode and an associated Instrumentation Laboratories, Inc., pH meter which had been calibrated with an aqueous buffer (pH 7), a reading of 11.9 was obtained.

B. Cells and Electrodes. For routine classical polarograms a Heath dropping mercury electrode apparatus (Model EUA-19-6) was employed with a 20-ml glass cell, a Pt wire as an anode, and a commercial Coleman Model 3-512 saturated calomel electrode as the reference electrode. This reference electrode was bridged to the solution being measured through solutions of 1 *M* KCl in H_2O and either 1 *M* *n*-Bu_4NClO_4 or 0.5 *M* *n*-Pr_4NClO_4 in DMF contained in polyethylene tubing and separated by plugs of porous Vycor glass (Corning Vycor No. 7930). Potential scanning and voltage and current measurements were performed with a Heath polarography module (Model EUA 19-2), operational amplifier (Model EUA-19B), amplifier stabilizer (Model EUA-19-4), and recorder (Model EU-20V). The maximum pen excursions were used for current measurements. Half-wave potentials measured with this apparatus are reported to the nearest 0.01 V and are estimated to be in error by less than ±0.1 V.

For more accurate classical polarographic measurements and for cyclic voltammetry, a 5-ml all-glass cell was fitted with inlet tubes to pass N_2 through or over the solution, an anode constructed from a 4 cm × 0.7 mm diameter Pt wire welded to tungsten and sealed into a Pyrex tube, and a salt bridge constructed from Pyrex glass tubing fitted with porous glass plugs (Corning Vycor No. 7930) in Teflon tubes and filled with 0.1–0.4 *M* *n*-Pr_4NClO_4 in DMF or HMP and aqueous 1 *M* $NaNO_3$.[50] This salt bridge was connected to a saturated calomel electrode of conventional design (Hg area, 1.1 cm^2). A dropping mercury electrode was constructed with a capillary drawn from 2-mm i.d. capillary tubing. With a Hg height of 44.2 cm, the capillary had a flow rate of 1.54 mg/sec and a drop time of 2.43 sec (aqueous 0.1 *M* KCl, open circuit). The aforementioned Heath apparatus was used for voltage and current measurements. The potentials were measured to 1 mV with a digital meter (United Systems Corp, Series 180). For accurate current measurements, the cathodic potential was advanced in increments of 30 mV and current–time curves were plotted on a storage oscilloscope (Tektronix RM 564 fitted with a differential amplifier, type 2-A63, and a time-base amplifier, type 2-B67) and the current was read after a droplife of 1 sec. The polarography module reference potential, the digital meter, and the oscilloscope were all calibrated with another digital voltmeter which had in turn been calibrated against a Weston cell. The current measurements were calibrated from measurement of potential differences across appropriate precision resistors. Polarographic reduction of an aqueous solution of $BaCl_2$ (1.1×10^{-3} *M*) and Et_4NI (0.100 *M*) at 27° gave $E_{1/2}$ −1.937 V (lit.[51] −1.940 V), $\Delta E/\Delta \log (i/i_d - i)$ 0.034 V (calcd 0.030 V). The half-wave potentials measured with this apparatus are reported to the nearest 0.001 V and we believe them to be in error by no more than ±0.01 V.

Stationary electrodes for cyclic voltammetry were prepared by joining Pt wire (0.4-mm diameter) to Ag wire (0.5-mm diameter) by melting in a small flame. The Pt wire was then heated rapidly in an air-H_2[52] flame until it melted to form a sphere (typical diameter, 1.25 mm). The Pt shank of this sphere was sealed into a soft glass (Kimble No. R-6) tube. For most measurements the Pt sphere was coated with Hg by heating the Pt sphere to red heat in an air-H_2[52] flame, cooling, and dipping into Hg. The cell resistances (Table V) were measured by connecting a sine-wave generator (Heath EUW-27) and a precision variable resistance (General Radio 602-N) in series with the appropriate cell electrodes. Voltage drops across a known resistance and the electrodes, measured with the oscilloscope, were used to calculate the resistance values after the frequency of the sine wave had been increased to the point (usually 4–8 kHz) where resistance was independent of frequency.

From these resistances the potential and current correction factors were calculated from the data of Nicholson.[53] Taking *R* as 50 ohms, at scan rates (ν) less than 20 V/sec, the corrections were negligible; at a scan rate of ν = 100 V/sec, the ir drop was 20 mV and (measured *i*p)/(true *i*p) = 0.95.

The triangular waves for cyclic voltammetry, generated with a Chemtrix, type 800, wave form source, were applied to the aforementioned Heath polarography module and the current-potential curves were displayed on the storage oscilloscope from which they were photographed with a Polaroid camera. A simple voltage offset unit was connected in series with the horizontal axis of the oscilloscope to permit use of the entire oscilloscope screen for potential sweep measurements. For each set of cyclic scans, the horizontal axis (potential values) of the oscilloscope trace was calibrated by superimposing spots corresponding to known potentials supplied from the calibrated potential source in the polarography module. The vertical axis (current measurement) was

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(46) See C. D. Ritchie and G. H. Megerle, *J. Amer. Chem. Soc.*, **89**, 1447 (1967).

(47) (a) N. C. Deno and H. E. Berkheimer, *J. Org. Chem.*, 28, 2143 (1963); (b) Y. H. Inani and J. B. Ramsey, *J. Chem. Phys.*, 31, 1297 (1959).

(48) G. A. Forcier and J. W. Olver, *Anal. Chem.*, 37, 1447 (1965).

(49) (a) M. Schütze, *Angew. Chem.*, 70, 697 (1958); (b) Badische Anilin- & Soda-Fabrik AG, Technical Bulletin, "BTS Catalyst."

(50) The use of aqueous $NaNO_3$ rather than KCl avoided precipitation of $KClO_4$ (and a resultant high impedance) in the porous glass plug separating the aqueous and nonaqueous portion of the salt bridge. See B. McDuffie, L. B. Anderson, and C. Reilley, *Anal. Chem.*, 38, 883 (1966).

(51) I. Zlotowski and I. M. Kolthoff, *J. Amer. Chem. Soc.*, **66**, 1431 (1944).

(52) Use of a gas flame would favor formation of platinum carbide.

(53) R. S. Nicholson, *Anal. Chem.*, 37, 667 (1965).

Table VI. Products from the Controlled Potential Reduction of the Ketone **11** with Various Catholytes

Solvent	Supporting electrolyte (concn, M)	Electricity, faradays/mol	Recovered **11**, %	Product yields, % (based on unrecovered **11**)	
				25	**24**
Anhydr DMF	n-Pr_4NClO_4 (0.2)	1.2	7	15	30
5.5 M H_2O in DMF, pH ~9	n-Pr_4NClO_4 (0.2)	1.0	12	10	55
5.5 M H_2O in DMF, pH ~13	n-Pr_4NClO_4 (0.2)	1.0	4	5	60
Anhydr HMP	$LiClO_4$ (0.1)	0.65	57	10	45

calibrated from measurement of the potential drop across precision resistors.

The $E_{1/2}$ values from classical polarography for a representative series of enones[54] are listed in Table I.

These data (Table I) were obtained with ketone concentrations in the range 5×10^{-4}–10^{-3} M and 0.1 M n-Pr_4NClO_4 as the supporting electrolyte. Analysis (glpc, TCEP column) of the crude neutral product recovered from the DMF solution of the *cis*-ketone **14**, both before and after polarography, indicated that less than 2% of the *cis*-ketone **14** had isomerized to the *trans*-isomer **11**.

To prepare pivalalacetophenone for polarographic measurement, 22.4 g (0.26 mol) of pivaldehyde was condensed with 28.9 g (0.24 mol) of acetophenone according to the procedure of Wiberg and Rowland[55] to yield 28.6 g of crude product, bp 86–97° (0.1–0.5 mm) [lit.[58] bp 98–99° (0.8 mm), $n^{25}D$ 1.5248]. This crude product contained (glpc, silicone, no. 710) both the desired unsaturated ketone (ret time 18 min) and a more slowly elected (23 min) unidentified impurity which was not easily separated by fractional distillation. A pure sample of the **pivalalacetophenone** was collected (glpc) as a colorless liquid: ir (CCl_4) 1675, 1670 (sh), and 1655 (sh) cm^{-1} (conj C=O) and 1620 cm^{-1} (conj C=C); nmr (CCl_4) δ 7.2–8.1 (5 H, m, aryl CH), an AB pattern (J = 17 Hz) with estimated line positions of 6.63 and 6.92 (2 H, *trans* CH=CH), and 1.12 (9 H, s, $(CH_3)_3C$).

The half-live values for the radical anions derived from a representative series of enones[54] are listed in Table III. Typical displays of data are illustrated in Figure 2. Where both anodic (i_{pa}) and cathodic (i_{pc}) currents could be observed, the scan rates (ν) where $i_{pa}/i_{pc} = 0.50$ are listed with the values of the half-wave potential ($E_{1/2}$), the switching potential (E_λ), and the total magnitude of potential change, $\Delta V = [(E_{pc} - E_\lambda) + (E_{pa} - E_\lambda)]$. The half-lives listed in Table III were calculated from these values by the two procedures described in the Discussion. For certain phenyl-substituted compounds where two cathodic peaks were observed but the anodic peak could not be measured, the half-life of the radical anion (corresponding to the first peak) was estimated to be the time (from values of ν and ΔV between the cathodic peaks) when i_{pc} (peak 1) = $2i_{pc}$ (peak II). In cases where neither of these procedures was appropriate, a maximum or minimum half-life of the radical anion has been estimated. For all measurements in DMF, the concentration of the supporting electrolyte (n-Pr_4NClO_4) was 0.5 M; for measurements in HMP the concentration was 0.1 M.

Controlled Potential Electrolyses. A. Apparatus. The previously described three-compartment cells[27] of various sizes were used with a stirred Hg-pool cathode (area, 38.5 cm^2 or 3.8 cm^2) and a Ag wire anode. A typical value for the anode–cathode resistance of these cells containing 0.1 M n-Pr_4NClO_4 in DMF was 900–1900 ohms; for the cathode–reference a typical resistance was 6.5 ohms. The anolyte was 0.2 M Et_4NBr in either DMF or DMF–H_2O (9:1, w/w). The previously described saturated calomel electrode fitted with appropriate salt bridges to the cathode compartment served as a reference electrode; the potential of the cathode (*vs.* sce) was monitored with a vacuum tube voltmeter. The cell current was supplied from one of several conventional, variable dc potential sources and the cathode–reference potential difference was maintained either by continuous manual adjustment during the electrolysis or by use of a feedback amplifier circuit. A gas coulometer, fitted with Pt electrodes and filled with aqueous 0.1 M hydrazine sulfate,[28] was placed in the circuit to measure the total current passed, and the electrolyses were judged to be complete when the rate of gas evolution in this coulometer became 1–3% of the initial value.

B. Preparative Electrolysis of Ketone 11. The ketone **11** (500 mg or 2.97 mmol) was dissolved in 150 ml of a catholyte prepared from 12.0 g of n-Pr_4NClO_4, 180 g of DMF, and 20 ml of aqueous 10% n-Pr_4NOH. This solution (0.2 M in salt and 0.05 M in base, pH ~13) was electrolyzed at −2.2 V (*vs.* sce, initial current 60 mA). After 2.3 hr, when gas evolution (49.4 ml or 1.00 Faraday/mol) had become negligible, the catholyte was removed and diluted with H_2O. The organic product which precipitated was collected, dissolved in Et_2O, washed with H_2O, dried, and concentrated to leave 0.45 g (90%) of the crude racemic dimer **24**, mp 112–117°. Recrystallization from methanol afforded 0.29 g (58%) of the dimer as white needles, mp 124–125°, identified with the previously described sample by mixture melting point and by comparison of glpc retention times. The mother liquor from the crystallization contained (glpc, silicone SE-52) small amounts of the reduction products **24** and **25** as well as two unidentified components with retention times intermediate between **24** and **25**.

A comparable reduction of 500 mg of the ketone **11** was performed in 150 ml of a catholyte prepared by adding 1.21 g of H_3BO_3 to 200 g of the previously described catholyte. This solution (0.05 M in base and 0.1 M in H_3BO_3, pH ~9) was electrolyzed at −2.2 V (*vs.* sce, initial current 60 mA) for 2 hr (1.06 faradays/mol) and subjected to the previous isolation procedure to give 0.45 g of crude product, mp 102–112°, which was recrystallized (MeOH) to separate 0.30 g (60%) of the dimer **24**, mp 124–125°. The electrolysis in the alkaline catholyte (pH 13) was repeated using a solution of n-Pr_4NOD in D_2O (from n-Pr_4NCl, Ag_2O, and D_2O). The racemic dimer, mp 126–156°, isolated in 50% yield, was found to contain (mass spectral analysis) 12% d_1, 62% d_2, 22% d_3, and 4% d_4 species. The nmr and mass spectra of the sample indicated that the bulk (if not all) of the deuterium was located at the carbon atoms α to the carbonyl group; the mass spectrum of the sample contained an abundant fragment peak at m/e 240. The corresponding peak is found at m/e 239 in the nondeuterated dimer **24** and at m/e 241 in the β,β-dideuterio dimer **31**. The assignment of this peak to fragment remaining after loss of t-$BuCOCH_2\cdot$ from the molecular ion is indicated by the presence of a metastable peak at m/e 169.0 (calcd $239^2/338 = 169.0$).

A series of small-scale reductions was carried out employing the catholytes indicated in Table VI. After the catholyte had been diluted with H_2O, it was extracted repeatedly with CCl_4. After the CCl_4 solution had been washed with H_2O, dried, and concentrated, the residual crude product was mixed with a known weight of p-di-t-butylbenzene (an internal standard) and analyzed by glpc with equipment previously calibrated with known mixtures of authentic samples. On one glpc column (silicone gum, SE-52 with programmed temperature rise) the retention times were: ketones **11** and **25** (not resolved), 8.0 min; p-di-t-butylbenzene, 15.1 min; and dihydrodienes **24** and **30** (not resolved), 33.4 min; in several crude reduction mixtures minor unidentified peaks were also noted at 3.9, 10.8, 24.0, and 25.3 min. With the second glpc column (silicone fluid, no. 710) the retention times of the monomeric ketones were **25**, 19.4 min and **11**, 21.2 min. The results of these analyses are summarized in Table VI. The nmr spectrum (100 MHz) of each of these product solutions was examined to determine the maximum amount of the *meso*-dihydrodimer **30** which could be present.

The positions of the t-butyl group singlets in the nmr for the various components of the mixtures are: p-di-t-butylbenzene, δ 1.31; unsaturated ketone **11**, 1.08 and 1.10; saturated ketone **25**, 0.90 and 1.12; racemic dimer **24**, 0.72 and 1.13; *meso* dimer **30**, 0.83 and 1.15. Thus, the ratio of areas under the peaks at δ 0.72 and 0.83 provided a measure of the amount of *meso*-dimer **30** present in the mixture of dihydrodimers **24** and **30**. For the reductions summarized in Table VI, the *maximum amount* of *meso*-dimer **30** which could be present in the dihydrodimer mixture (**24** + **30**) was: anhydrous DMF, 5% **30**; 5.5 M H_2O in DMF, pH ~9, 5% **30**; 5.5 M H_2O in DMF, pH ~13, 4% **30**; anhydrous HMP, 7% **30**.

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[54] The preparation and characterization of certain of these enones are described in ref 3.

[55] K. B. Wiberg and B. I. Rowland, *J. Amer. Chem. Soc.*, 77, 1159 (1955).

A comparable electrolysis was performed at a potential of -2.0 to -2.3 V with an MeCN solution which contained the ketone **11** (0.059 *M*), n-Pr_4NClO_4 (0.1 *M*), and H_2O (1.64 *M*). After the current became negligible 1.30 faradays/mol), the catholyte was diluted with H_2O and extracted with CCl_4. After the CCl_4 solution had been dried and concentrated, the crude product contained (glpc, carbowax 20M); the monomer **25** (*ca.* 15%, ret time, 2.2 min), unknown A (*ca.* 4%, 2.7 min), unknown B (*ca.* 9%, 5.1 min), unknown C (*ca.* 3%, 26 min), unknown D (*ca.* 4%, 30 min), and the dimer **24** (*ca.* 65%, 34.5 min). Collected (glpc) samples of the monomer **25** and dimer **24** were identified by comparison of ir spectra and glpc retention times. From an analogous preparative experiment the dimer **24** was isolated in 54% yield as needles from MeOH, mp 124–125°.

C. Solutions of the Radical Anion from Ketone 11. Solutions of one of the ketones **11–14** (1×10^{-3} *M*) and n-Bu_4NClO_4 (0.1 *M*) in DMF or MeCN were degassed by alternate freezing and thawing cycles under reduced pressure in the side arm of an electrolytic cell which could be placed in the microwave cavity of an epr spectrometer (Varian Model E-3). The working portion of the cell consisted of a piece of 3-mm o.d. Pyrex glass tubing with an Hg cathode at the bottom and an Ag wire anode at the top. The minimum dc potential (measured with a vacuum tube voltmeter) required to obtain a stable epr signal was applied to the cell and the esr spectrum of the solution just above the Hg cathode was scanned. Alternatively, a solution of 2–5 mg of the ketone and 50 μl. of Na–K alloy were mixed in 1–2 ml of a THF–DMF solution (2:1, v/v) contained in a 4-mm quartz tube and the epr spectrum of the resulting solution was determined. Examples of the epr spectra obtained by these methods are illustrated in Figure 1. The *g* values were determined by comparison with the epr spectrum of a solution of diphenylpicrylhydrazyl.[56]

Solutions of the radical anions from ketones **11–13** in anhydrous DMF containing 0.2 *M* in n-$PrNClO_4$ could also be obtained by electrolysis (-2.4 to -2.5 V *vs.* SCF, initial current <10 mA) in the three-compartment cell described in a previous section. When strict attention was paid to maintaining an O_2-free catholyte, the catholyte solution slowly aquired a yellow-brown color. If passage of current through the cell was interrupted, a potential of -2.22 V was observed between the cathode and the reference electrode so long as the yellow-brown color remained. It was possible to transfer these solutions through a glass or stainless steel cannula from the cathode compartment to a cell for measurement of electronic spectra or to 3-mm o.d. tubes for measurement of esr spectra. The epr spectra obtained from solutions of ketones **11–13** corresponded with those obtained by the previously described electrolysis in the microwave cavity of the epr spectrometer. When samples of the *cis*-ketone **14** were added to the solutions in which a small amount of the *trans* isomer had been reduced and the paramagnetic product then allowed to decay, the *cis*-ketone **14** was practically completely isomerized (glpc analysis) to the *trans*-isomer **11** in periods of 15 min or less.

A solution 14.9×10^{-3} *M* in the ketone **11** was electrolyzed until the associated gas coulometer indicated that the amount of radical anion formed would correspond to a concentration of 1.98×10^{-3} *M*. The spectrum of this DMF solution had a peak at 435 mμ ($A = 0.76$) corresponding to a minimum value for ϵ of 400 if no decomposition of the radical ion had occurred. The spectrum also exhibited intense end absorption at *ca.* 350 mμ. The extinction coefficient gradually decreased and no absorption was observed at 435 mμ after 24 hr. By observing the intensity ratio of the epr signal principal doublet with scanning times of 2, 9, and 17 min and assuming this ratio to be unity if no decay of the radical occurred, a rate constant for the loss of the radical anion could be estimated. From the epr spectra a first-order rate constant at 27° of $1.0 \pm 0.2 \times 10^{-3}$ sec^{-1} ($t_{1/2} = 690$ sec) was calculated; a rate constant of $1.0 \pm 0.1 \times 10^{-3}$ sec^{-1} was calculated for the α-deuterio ketone **12**. From the rate of disappearance of the 435-mμ absorption of the electronic spectrum with time at 22.5°, the following first-order rate constants were calculated: with 0.1 *M* n-Pr_4NClO_4 in DMF, 4.4×10^{-4} sec^{-1}; with 0.2 *M* n-Pr_4NClO_4 in DMF, 4.2×10^{-4} sec^{-1}; with 0.1 *M* n-Pr_4NClO_4 in HMP, 8.6×10^{-4} sec^{-1}. Both sets of measurements are consistent with a decay process which is first order in the anion radical over a range of three half-lives.

A solution of 52.0 mg of the ketone **11** in 20 ml of 0.2 *M* n-Pr_4NClO_4 in DMF was electrolyzed at -2.4 to -2.5 V until 1.05 faradays/mol of electricity had passed through the cell. The brown catholyte solution was allowed to stand under N_2 for 12 hr to permit complete decay of the radical anion and then the solution was partitioned between H_2O and Et_2O. After the ether extract had been washed (aqueous $NaHCO_3$), dried, and concentrated, an internal standard (p-dibromobenzene) was added and the product was analyzed (glpc, TCEP column). The calculated yields were: starting ketone **11**, 20%; monomer **25**, 7%; dimer **24**, 73%.

After a solution of the α-deuterio ketone **12** (93% d_1 and 7% d_0 species) had been partially electrolyzed (0.6 faraday/mol) in the same manner, the epr spectrum of a portion of the solution was shown to correspond to the spectrum illustrated in Figure 1 (spectrum D). The remainder of the solution was partitioned between H_2O and pentane and the starting ketone was collected (glpc, TCEP column). This sample contained 48% d_1 species and 52% d_0 species. The ir spectrum of the sample showed it to be a mixture of ketones **11** and **12**. To demonstrate the presence of relatively rapid electron exchange between the radical anion and the starting ketone in this system, a solution containing 0.175 mmol of the nondeuterated ketone **11** was electrolyzed (0.56 faraday/mol). The electrolysis was stopped and 0.165 mmol of the β-deuterio ketone **13** was added to the brown solution. After the resulting mixture had been stirred for 1 min, a portion of the solution was transferred to a 3-mm tube and the epr spectrum was determined within 20 min. The epr spectrum was a composite of an approximately equal mixture of the radical anions whose spectra are illustrated in Figure 1 (curves A and B). The relative intensities of the epr lines did not change with time.

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(56) Further details of these measurements are available in the Ph.D. Dissertation of Nancy H. Kolodny, Massachusetts Institute of Technology, Cambridge, Mass., June 1969.