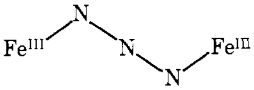

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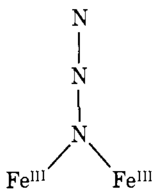
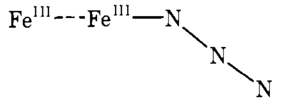


VII



VIII

hemerythrin, and that the correct structures contain individual O and N atoms in nonequivalent positions.[10-12]

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(9) E. B. Wilson, J. C. Decius, and P. C. Cross, "Molecular Vibrations", McGraw-Hill, New York, N.Y., 1955. For structures I, III, and IV, Fe-O-O angles of 120° were assumed. For all structures, a bond distance of 1.9 Å was assumed for Fe-O and 1.45 Å for O-O.

(10) The observed splittings of $\nu_{\text{Fe-O}}$ and of $\nu_{\text{N}\equiv\text{N}}$ are too large to be ascribed to hydrogen bonding to, or protonation of, one of the O atoms in I, II, or V or one of the N atoms in VI. Furthermore we detect no frequency shifts for $\nu_{\text{N}\equiv\text{N}}$ or $\nu_{\text{Fe-N}}$ with azidomethemerythrin dissolved in D_2O in place of H_2O.

(11) It is obvious that unsymmetrically-labeled O_2 could also be used to delineate the disposition of oxygen atoms of dioxygen bound by hemocyanin.

(12) This investigation was supported in part by Grant HL-08299 from the National Heart and Lung Institute, U.S. Public Health Service.

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High Yield Generation of a Persistent, Saturated Lithium Ketyl in Solution. Characteristic Reactions and Identification by Electron Spin Resonance

Sir:

The classical, still much used method for reducing saturated ketones to alcohols is reduction by means of alkali metals in the presence of proton sources.[1] The mechanism proposed by House for these "dissolving metal reductions" is now generally accepted. In essence, it establishes the sequence, (1) electron transfer to give a ketyl, (2) protonation of the ketyl to give a ketyl radical, and (3) electron transfer to the ketyl radical; dimerizations compete with steps 2 and 3. The ketone dianion intermediates proposed some time ago by Barton[2] are now excluded. In acidic media, the location of the protonation step is to some extent uncertain and, conceivably, important reactions of the ketyls could proceed undetected.

In principle, the lifetime of the ketyls should be longer if the reduction were carried out in nonacidic media. Suitably substituted ketyls should be persistent[3] and it should be possible to show whether further reduction is possible. Study of the chemistry of ketyls in nonacidic media could begin with that of the reactions of persistent ketyls with a variety of reagents.

Apart from the early, promising experiments of Favorski and Nazarov,[4] this approach has been neglected although the formation of ketyls from a number of aliphatic ketones and alkali metal mirrors has since been observed in ESR spectroscopic studies.[5] Later chemical studies of aprotic systems are mainly oriented towards favoring the dimerization of the ketyls.[1]

To bridge the gaps between these sets of data, we have combined ESR and chemical studies of several aprotic systems. Here we wish to report that the reaction between 2,2,6,6-tetramethylcyclohexanone (**1**) and excess lithium in unactivated form in THF at ca. −75° leads to near-quantitative formation of "stable" (−75°) solutions of the corresponding lithium ketyl ($\mathbf{1}\cdot^{-}\mathrm{Li}^{+}$), but does not proceed further, as indicated by chemical reactions ascribed to $\mathbf{1}\cdot^{-}\mathrm{Li}^{+}$, and as confirmed by observation of $\mathbf{1}\cdot^{-}\mathrm{Li}^{+}$ by ESR.

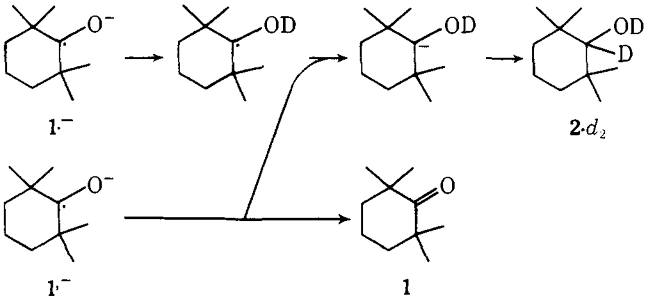
The following considerations determined the choice of the alkali metal, the solvents, and of the ketonic substrate. Suspensions or solutions of lithium metal in donor solvents are the most strongly reducing chemical systems. Moreover, lithium can form strong covalent bonds with carbon; ketone dianion-like species with a covalent C–Li bond should be more stable than true dianions.[1] We use ethers with moderate donor properties such as THF or 1,2-dimethoxyethane (DME) which provide solvation of contact-paired and covalently bound lithium, but leave these C–Li bonds intact; these ethers resist well to abstraction of protons and hydrogen atoms. We find that saturated ketones in THF solution readily react with lithium pieces[6] at ca. −75°. For this first study, we chose a highly hindered ketone in order to slow down bimolecular reactions of derived anions, such as reactions with the medium and dimerization (of the ketyl). In order to exclude the possibility of disproportionation,[7] we used a ketone without hydrogen atoms in the α-positions.

Solutions of **1** (ca. 0.2 M) in THF were stirred at ca. −75° with a large excess (20–50 g-atoms per mole of **1**) of lithium under argon. After stirring for varying periods (10 min to 10 h),[8] the remaining lithium was removed, and the cold (−75°) solutions were quenched with deuterium oxide.[9] Workup with water and distillation of the hydrolysates furnished mixtures of **1** and of the corresponding α-deuterated alcohol **2**-*1-d* (Scheme I) in 88–92% combined yield.[10] The molar ratio of **1**:**2** in the hydrolysates had an essentially constant value of unity (0.97–1.10) for contact times (THF solution at −75°/lithium) of 1 h and up to 10 h. The aqueous phases of these hydrolysates contained 1.05–1.10 mol of lithium hydroxide per mole of **1** added initially. After contact times of $<\sim 1$ h the hydrolysates contained **1** and **2** in ratios >1. The deuterium content of the **2**-*1-d* in the hydrolysates did not depend on the contact time and was 0.88–0.93 D atom per molecule.[11]

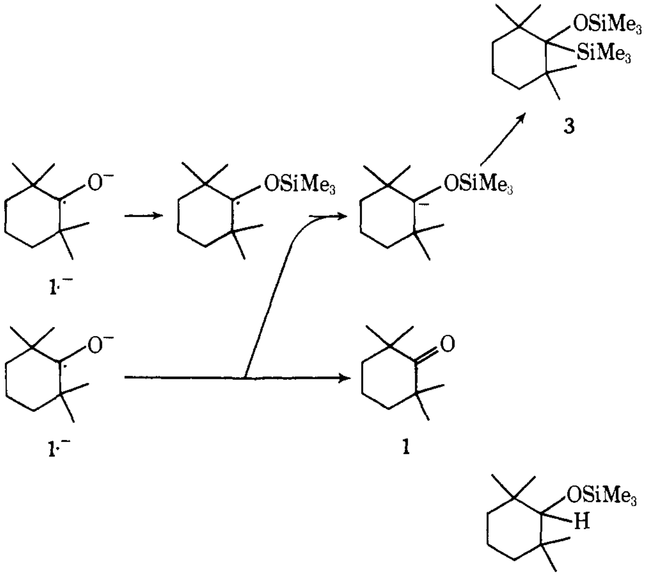
The presence of ketone **1**, alcohol **2**, and lithium hydroxide in equimolar amounts in the hydrolysates defines the overall level of reduction of the species in THF solution as that of the lithium ketyl $\mathbf{1}\cdot^{-}\mathrm{Li}^{+}$. The only sound interpretation is that only this species is present in significant amounts.[12] We conclude that $\mathbf{1}\cdot^{-}\mathrm{Li}^{+}$ is formed in high yield (the equilibrium $\mathbf{1} \rightleftharpoons \mathbf{1}\cdot^{-}\mathrm{Li}^{+}$ lies far on the right) and is persistent in solution at −75°. In particular, $\mathbf{1}\cdot^{-}\mathrm{Li}^{+}$ is not further reduced to any significant extent. Protonation of $\mathbf{1}\cdot^{-}\mathrm{Li}^{+}$ induces a disproportionation, as predicted by House's mechanism (Scheme I, reaction with deuterium oxide, exchange on workup gives **2**-*1-d*).

Reaction of **1** with lithium in THF at −75° for 3 h as before, treatment of the solution with an excess of trimethylsilyl chloride at −75° after removal of the remaining lithium, and stirring for 4 h at −75°, followed by rapid hydrolytic workup and distillation, gave a mixture of **1** and its bis(trimethylsilyl) derivative **3** (Scheme II), in a ~1.2:1 molar ratio, and in addition a little of the trimethylsilyl ether **4**, in ~75% combined yield.

Scheme I



Scheme II

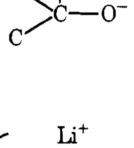


4

Trimethylsilylation of **1**·$^-$Li$^+$ apparently also induces a disproportionation.[11] We propose a mechanism (Scheme II) which is formally analogous to Scheme I. Equivalent mechanisms involving ketyls as first intermediates can now be inferred for the corresponding three component reactions.[13]

The extensive ESR spectroscopic studies[5] of saturated ketyls in aprotic solvents show that the ketyls exist as contact ion quadruplets and higher contact ion clusters in these media. The former can be identified unambiguously, giving rigid media spectra characteristic of biradicals.

Solutions obtained as described (reaction between **1** and lithium in THF for ~3 h, separation from remaining lithium) showed a strong ESR signal without hyperfine structure at −75°; an unresolved spectrum was previously reported for the corresponding potassium ketyl **1**·$^-$K$^+$ (potassium mirror/THF).[5f] Spectra of our frozen solutions at 77 K showed the presence of a triplet species (transitions $\Delta M = 1$ and $\Delta M = 2$) with zero-field parameters $E/hc \approx 0$ and $D/hc = 0.0197$ cm^{-1} ($r = 5.1$ Å). On the basis of Hirota's work,[5e] this biradical can be identified as the contact ion quadruplet (**1**·$^-$Li$^+$)$_2$,[14] with bridging lithium cations and a mutually perpendicular arrangement of the



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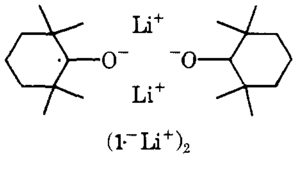
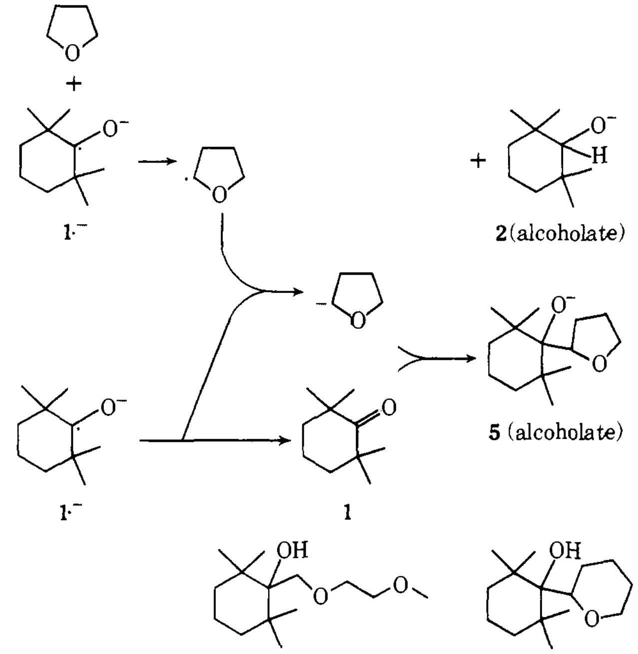


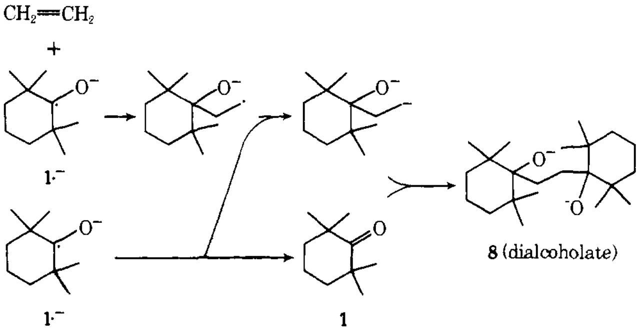
(1·$^-$Li$^+$)$_2$

Scheme III



6 **7**

Scheme IV



The spectra show an additional, intense central peak which can be assigned to higher contact ion clusters[5e] (**1**·$^-$Li$^+$)$_n$. On warming to −100° or above, only the structureless, central peak remains; on warming further, to ~0° or above, this peak disappears within ~30 min.

Combination of the qualitative identification by ESR with the evidence of quantitative chemical reactions which require mechanistic interpretation, completes the identification of **1**·$^-$Li$^+$. All of its reactions (and those of lithium ketyls in general) probably involve associated, lithium-bridged species directly.[15] In the hydrolysis, for instance, monoprotonation of a dimer probably triggers off extremely rapid disproportionation within the pair (Scheme I).[9] In this context, solution thermolyses of **1**·$^-$Li$^+$, and the reaction of **1**·$^-$Li$^+$ with ethylene are of interest.

ESR showed solutions of **1**·$^-$Li$^+$ to be unstable at higher temperatures, as mentioned. Warming THF, DME, or tetrahydropyran solutions to −25° or above, and subsequent hydrolysis, gave the solvent-"adducts" **5**, **6**, and **7**, respectively (Scheme III), along with **2** and **1**. **1**·$^-$Li$^+$ apparently abstracts a hydrogen atom from the solvent, and part of the solvent-derived radicals are then trapped by the remaining **1**·$^-$Li$^+$, probably via prior electron transfer (Scheme III; cf. Schemes I and II). The alcoholate of **2** is also formed independently, and some of **1** is regenerated. Capture of the solvent-derived radicals is efficient because the initial concentration in **1**·$^-$Li$^+$ is high; thermolysis of **1**·$^-$Li$^+$ in THF at +3° (prepared as before at −75°) during 3.5 h, hydrolytic workup, and distillation afforded **1**, **2**, and, **5**, in ~1:5:2 molar ratios, in ~87% combined yield.

Reinvestigations of the work of Favorski and Nazarov[4] by Eberson[16] and by Bartlett et al.[17] suggest that saturated ketyls must have extraordinary reactivity towards ethylene. $\mathbf{1}\cdot^{-}\mathrm{Li}^{+}$ in solution indeed reacts cleanly with ethylene at −30° or above, to give the dialkoxide of the 1,4-diol **8** (Scheme IV). In addition, **1** and the alcoholate of **2** are formed; the formation of the solvent-"adduct" **5** (alcoholate) is suppressed. Thus reaction of $\mathbf{1}\cdot^{-}\mathrm{Li}^{+}$ prepared as before in THF at −75°, with a large excess (~15 equiv) of ethylene at −22° for 24 h, followed by hydrolysis and purification gave **1**, **2**, and **8** in ~3:2:3 molar ratios, in ~68% combined yield.

These experiments prepare the ground for the study of the reactions of transient ketyls in nonacidic media.[7]

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(6) Lithium rods (Metallgesellschaft, purity 99.4–99.8%) were hammered flat, etched to brilliance in methanol, and rinsed and cut into pieces in THF or DME.
(7) To our knowledge, a disproportionation of saturated ketyls has never been observed or considered. We have since discovered that lithium ketyls do undergo disproportionation. V. Rautenstrauch, manuscript in preparation.
(8) The color of the solution changed from colorless to light red-brown (~10 min), to dark brown (1–10 h).
(9) A large excess of deuterium oxide (ca. 23°) was added to the stirred, cold solutions. Alternatively, the cold solutions were poured into ice-cold water or aqueous acid. Clean disproportionation occurred under all conditions tried.
(10) Similar results were obtained when the reaction was carried out in DME at −48°, but $1\cdot^{-}\mathrm{Li}^{+}$ appears to be somewhat less stable under these conditions. We have mainly worked with THF solutions which remain mobile at ca. −75°.
(11) Small amounts of the alcoholate of **2** are apparently formed by reaction of $1\cdot^{-}\mathrm{Li}^{+}$ with (unlabeled) impurities in the medium. Trimethylsilylation of this alcoholate gives **4**.
(12) We exclude the presence of ternary mixtures of **1**, $\mathbf{1}\cdot^{-}\mathrm{Li}^{+}$, and the dianion $\mathbf{1}^{2-}2\mathrm{Li}^{+}$, of an equimolar mixture of **1** and $1^{2-}2\mathrm{Li}^{+}$, and of the pinacolate corresponding to $\mathbf{1}\cdot^{-}\mathrm{Li}^{+}$. We have never found any pinacol.[9] In classical experiments, "lithium benzophenone ketyl" has been shown to behave analogously; hydrolysis with aqueous base yields 1:1 mixtures of benzophenone and benzhydrol. However, the ketyl and the ketyl radical dimerize, and the pinacol is cleaved. Hydrolysis of dilithium benzophenone dianion gives benzhydrol only. For a recent discussion see L. S. Trzupek, T. L. Newirth, E. G. Kelly, N. E. Sbarbati, and G. M. Whitesides, *J. Am. Chem. Soc.*, **95**, 8118 (1973).
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(14) Hirota's zero-field parameters for the rigid medium spectrum (77 K, methyltetrahydrofuran) of the structurally similar contact ion quadruplet derived from hexamethylacetone (lithium mirror) are $E/hc \approx 0, D/hc = 0.0210\ \mathrm{cm}^{-1}$ ($r = 5.0$ Å).[5e] The half-field transition was not observed.
(15) For clarity this is not explicitly formulated in the schemes; lithium cations are omitted.
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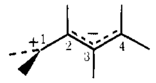
Coexistence of Two Oppositely Polarized Zwitterionic Forms on the Lowest Excited Singlet Surface of Terminally Twisted Butadiene. Two-Funnel Photochemistry with Dual Stereochemistry

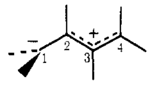
Sir:

The suggestion that certain photochemical rearrangements of hydrocarbons proceed through excited ionic intermediates was first made by Dauben.[1] For the photocyclization of butadiene to bicyclobutane[2] the orthogonal zwitterion I was proposed[1] as a primary intermediate. It has recently been shown[3] that the lowest excited zwitterionic states Z_1 and Z_2 of diradical species can indeed be strongly polarized. This *sudden polarization effect* occurs (a) if the overlap between the two radical sites is sufficiently weak and (b) if a dissymmetry exists between these two sites.[4] The high polarizability of the two zwitterionic states of ethylene had been predicted theoretically by Wulfman and Kumei.[5]



I

The sudden polarization effect was originally described in the following manner. For a given geometry, the lowest Z_1 state is polarized in one direction, and the upper neighboring Z_2 state is polarized in the opposite direction. In 90° twisted methylene-allyl with an arbitrary geometry (C_1C_2 = 1.50 Å, C_2C_3 = C_3C_4 = 1.40 Å), a minimal basis set calculation[6] gives the polarization shown in I for Z_1, while Z_2 adopts the polarization shown in II. Actually the favored polarization depends on the choice of basis set.



II

For the same geometry the polarization of the Z_1 and Z_2 states is reversed if an extended basis set[6] or polarization functions are used. Physically, however, such calculations are not too meaningful since the excited molecule, in either of the polarized forms I and II, will seek to optimize its energy by adopting the geometry most appropriate to that form. If the optimized geometries corresponding to I and II are sufficiently different, the form whose energy has been optimized should always lie, at its optimum geometry, *below* the form with the opposite polarization. The two optimized geometries should lie on the *same*, lowest singlet excited surface.

We have now carried out this dual geometry optimization for methylene-allyl in order to verify our assumption. The potential energy surface (Figure 1) for the lowest excited singlet state has indeed *two* minima[7] corresponding respectively to forms I and II in their optimized geometries. Form II lies lower in energy. The energies of the two wells differ by 9.2 kcal/mol, with an intermediate barrier of 6.6 kcal/mol between higher well I and lower well II. The energetic ordering of the wells is *independent of basis set.*[9] The figure also shows the optimized geometries of I and II and their charge distribution.

The photochemical implications of such a double-well potential are noteworthy. The presence of two wells allows the possibility of two distinct photochemical pathways for which the wells act as funnels.[10] If one well is much lower (10 kcal/mol, say) than the other, one pathway will predominate. If the two wells are relatively close in energy, the two paths should be competitive. Consider for instance the introduction of a terminal methyl group on the butadiene molecule (there are now four possible intermediate orthogonal methylene-allyl zwitterionic forms). We arbitrarily place II, 4-methyl at 0