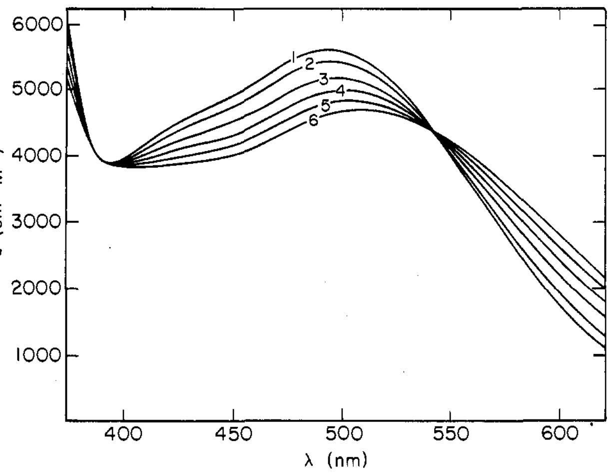

Figure 2. The visible spectrum of ferric enterobactin as a function of pH: 1, 7.29; 2, 5.66; 3, 5.11; 4, 4.80; 5, 4.53; 6, 4.23.

Table I

ligand	log K	log β_3	pM[a]
enterobactin	52		35.5
ferrioxamine B	30.6[b]		26.6
ferrichrome	29.1[b]		25.2
aerobactin	23.1		23.3
tiron		45[c]	19.5
2,3-dihydroxyphenylacetic acid		43.9[c]	15[d]
catechol		43.7[c]	15.8[d]
4-nitrocatechol		43.3[c]	23.4
2,3-dihydroxy-*N*,*N*-dimethylbenzamide		40.2[e]	15[d]

[a] Calculated for 10 μM ligand, 1 μM iron(III), at pH 7.4. [b] $K = [ML]/([M][L])$; values are from ref 11. [c] $\beta_3 = [ML_3]/([M][L]^3)$; values are from ref 3. [d] Calculated pM is below the lower limit determined by the K_{sp} of ferric hydroxide, indicating precipitation of iron under these conditions. [e] Value is from ref 2.

$$K_{\mathrm{Fe(Hent)}} = \frac{[\mathrm{Fe(Hent)}^{2-}]}{[\mathrm{Fe(ent)}^{3-}][\mathrm{H}^+]} = 10^{4.89(6)} \quad (4)$$

This protonation equilibrium was included in the calculation of K^* described above, and its implications will be discussed in a later full report.

The iron(III) stability constants of some hydroxamate siderophores and several bidentate catecholate ligands are listed in Table I. Also listed are pM values (pM = $-\log\,[\mathrm{Fe(H_2O)_6}^{3+}]$) for iron–ligand solutions at equilibrium under the conditions specified in Table I. The log β_3 values of the catecholate ligands are in the range of 40–45 and are much larger than the formation constants of the hydroxamate siderophores. However, the pM values show that the hydroxamate ligands are much more effective at sequestering ferric ion under the prescribed conditions. This is due primarily to the high basicity of the catecholate ligands, which results in significant competition by hydrogen ion, even at neutral pH. A second factor which is important in dilute solutions is the third-order dependence of β_3 on the free ligand concentration. This reduces the relative effectiveness of bidentate ligands compared with that of compounds forming 1:1 iron complexes.

The log K_f value of enterobactin is the largest formation constant of any iron chelate yet reported and is 7–12 log units larger than the log β_3 values of the bidentate catecholates. Also, since enterobactin forms 1:1 ferric complexes, its effectiveness is not so adversely affected by dilution. As a result of these two factors, the pM value of enterobactin is many log units higher than any of the other ligands listed in Table I. Thus it is clear that enterobactin is a unique and very promising model on which to base future efforts toward the design of more effective iron sequestering agents.

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Wesley R. Harris, Carl J. Carrano, Kenneth N. Raymond*
Department of Chemistry, University of California
Berkeley, California 94720

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Metal Alkyls as Precursors for Polylithium Organic Compounds. A High Yield Synthesis for "C_2Li_6"

Sir:

Polylithium organic compounds have great potential as reagents; more recently, polylithium organic compounds are emerging as one of the most novel and significant areas of investigation with respect to structure and bonding in organic chemistry. We have predicted that the polymeric structures of organic and inorganic polylithium compounds in the solid state may rival the boron hydrides in their complexity and novel bonding properties.[1] The idea that the structures of polylithium compounds as isolated species in the gas phase will be fascinating and most unusual has been more concretely and elegantly illustrated by the ab initio calculations and predictions of Schleyer and Pople and co-workers.[2] Their striking predictions range from bonding configurations of carbon atoms, which are nearly planar rather than tetrahedral, to a number of unusual cases of electron-deficient three-center bonding of lithium and carbon in the monomers. The first structure of a simple polylithium organic compound, "dilithiomethane", is in progress by Stucky and co-workers.[3]

Presently, the elucidation of the structures of polylithium compounds is extremely important. Our synthesis of polylithio compounds using lithium vapor[1,4–7] is complicated by problems in separation of products from the lithium matrix (lithium must be in excess to obtain the most highly substituted compounds) which is always present and from other polylithium species which are generated in the process such as lithium acetylide, C_2Li_2, and byproducts, such as lithium chloride and lithium hydride. A breakthrough in separations of this type is forthcoming.[8] A more difficult problem arises from the fact that, even though yields as high as 90% have been obtained from the lithium reactions,[4] in all previously reported cases the polylithium compounds have been obtained as a mixture of at least three such species. Separation of individual polylithium compounds is a much more demanding problem.

This communication describes a specific high yield synthesis of Li_6C_2 in which the product is obtained in 99% purity from the reaction

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Table I. Composition of Hydrolysis Products (Percent)[a]

	reactant						
	$(Et)_2Hg$	$(Et)_4Sn$	$(Et)_4Pb$	$(CH_3)_2Hg$[b]	$(CH_2I)HgI$	$(CF_3)_2Hg$	$(C_2H_3)_4Sn$
C_2H_5D	0	85	80	0	0	0	0
C_2D_6	99	10	9	43	72	46	23
C_2D_4	t	2	3	17	10	11	21
C_2D_2	t	3	8	40	18	31	56
C_3D_8	0	t	t	t	t	5	t
C_3D_6	0	t	t	t	t	7	t
C_3D_4	0	t	t	0	0	t	t

[a] t = trace. [b] A trace of CD_4, CHD_3, and CH_2D_2 were found.

$$12Li_{(g)} + Hg(C_2H_5)_2 \rightarrow 2C_2Li_6 + Hg$$

The chemistry of the reactions of metal alkyls with lithium vapor is also extremely interesting. A series of seven metal alkyls was selected for the study of the reaction sequence

$$Li\ (800\ ^\circ C) + M(R)_n \rightarrow nC_xH_yLi_z + M + LiH$$

Widely used techniques for making lithium alkyls involve reacting an organometallic compound of a metal less electropositive than lithium (especially tin, lead, and mercury) with either lithium metal or an alkyllithium reagent in an appropriate solvent. Extremely interesting would be the determination whether the lithium vapor reaction would simply produce the known alkyllithium compounds, such as methyllithium and ethyllithium from methyl and ethyl alkyls, or whether more extensive lithium substitution would occur.

The reactions were studied in the stainless steel reactor illustrated in Figure 1. The operation of a similar reactor system has been described previously.[4,7] In a 25-min reaction, ~11 g of lithium was vaporized at 800 °C from the Knudsen cell and reacted with 0.5 to 1 g of the metal alkyl which was admitted to the reactor through the inlet tube. The reactor was then opened under argon and the extremely reactive solid products from the cold finger, which had been cooled with liquid nitrogen, were removed under argon and carefully hydrolyzed with D_2O over a 1-day period on a vacuum line. The volatile products were separated by vacuum line fractionation from excess D_2O. The noncondensables (containing methane products and D_2O were analyzed by their high resolution mass spectra. The rest of the material was analyzed by GLC using a 10 m × ¼ in. Durapak phenyl isocyanate on Porasil C column. The individual compounds were identified by comparison of their retention times with those of known samples. The degree of deuteration was determined by low resolution mass spectra of the separated compounds and the identity of each species was confirmed by a high resolution mass spectrum. No ambiguous cases were found which required ^1H or ^{13}C NMR study. It has been previously shown[4,5] that the polylithium compounds such as CLi_4, C_2Li_6, and C_2Li_2, etc., react with chlorotrimethylsilane to give the expected substitution products and that the reaction of ethyllithium with chlorotrimethylsilane produces the monosubstituted trimethylsilylethane as indicated by a parent peak in the mass spectrum.

The course of the reactions are clear from the analysis of the composition of the hydrolysis products (see Table I) of the material removed from the cold finger of the reactor. The conversions in each reaction were over 25% and the yields are given in Table I for each hydrolysis product.

The reaction of ethyl organometallics is particularly interesting. Diethylmercury, as previously indicated, gives a 99% yield of the compound "C_2Li_6", whereas the tetraethyllead and tetraethyltin compounds produce predominantly the known compound, ethyllithium, and only a 10% yield of the completely substituted lithium compound. It is very interesting to note that no partially lithium-substituted ethanes, other than C_2H_5Li, were found on careful inspection of the hydrolysis products in the reactions of the three ethylalkyls. It seems to indicate that the lithium substitution reaction on ethane will go to completion once a second hydrogen atom is replaced, unless the initial reaction stops at the easily accessible radical reaction, simply bonding to the ethyl radical. The difference in products observed may be explainable by the varying tendencies of the organometallics to form radicals in contact with the high-temperature lithium vapor.

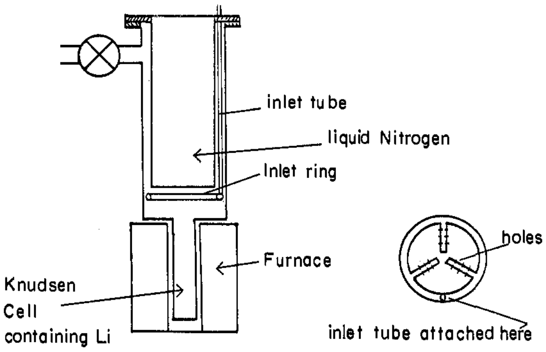

Figure 1. Improved reactor.

The methylalkyls and halogen-substituted methylalkyls exhibit more complex reactions. In all three reactions, the predominance of two carbon lithium compounds over simple substitution of the methyl radicals is clearly observed. The C_2Li_2, C_2Li_4, and C_2Li_6 species were probably formed by a combination of two partially lithium-substituted methyl radical or carbenoid species followed by further lithium substitution rather than by lithium attack on C_2H_6 formed by a coupling of the two methyl radicals. This process is unlikely as we have previously found lithium vapor to be unreactive toward alkanes, unless the alkane is vibrationally excited.[7] Such coupling reactions were also observed in the reaction of carbon tetrachloride with lithium.[4] The hydrolysis product from the $Hg(CH_2I)I$ reaction produces 72% C_2D_6.

A higher degree of unsaturation of the products of the reaction of $Hg(CF_3)_2$ is also observed along with a higher percentage of C_3 species, indicating that the reaction has a greater tendency to form chain products. A reasonable explanation would involve the ease of lithium fluoride elimination which causes an increase in the number of radical species available for coupling and polymerization reactions.

The reaction of tetravinyltin is interesting since the products are almost entirely two-carbon completely lithium-substituted species. This is reasonable since we have previously shown that the reactions of alkenes with lithium vapor are quite facile and produce preferential lithium substitution for the hydrogen on the unsaturated carbons.[7]

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Lawrence A. Shimp, Richard J. Lagow*
Department of Chemistry, University of Texas at Austin
Austin, Texas 78712

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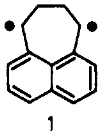
Biradicaloid Intermediates in Photochemistry: Spectroscopic and Kinetic Study of 1,4-Perinaphthadiyl and Related 1,8-Naphthoquinodimethanes

Sir:

Information regarding the electronic structure, energy, and reactivity of biradicaloid intermediates in their ground and low-lying excited states is scarce but essential for a mechanistic understanding of most photochemical[1] and many thermal reactions. We present such information for 1,4-perinaphthadiyl (**1**), a π,π biradical generated by a light-induced nitrogen elimination and studied by ESR and time-resolved absorption and emission spectroscopy in the range of 4–350 K. While first attempts to detect the optical spectrum of parent 1,8-naphthoquinodimethane (**2**) have failed,[2] the triplet state of both **1**[3] and **2**[4] has been identified by ESR spectroscopy, and Michl et al.[5] have recently reported optical and ESR spectra of 1,3-perinaphthadiyl (**3**). Our present results indicate that previous[3,5] determinations of the singlet–triplet energy gap of **1** and **3** are erroneous and that the absorption and emission spectra attributed to singlet **3**[5] should be reassigned.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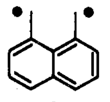
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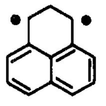
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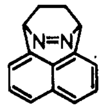
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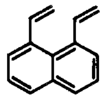
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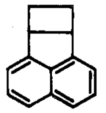
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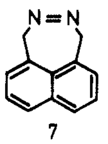
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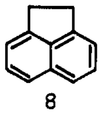
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Prolonged irradiation of the azo compound **4**[3] in rigid glasses at 77 K results in a quantitative conversion into 1,8-divinylnaphthalene (**5**). Analysis of the progressive changes in the absorption spectrum of a 10^{-4} M solution by the method of Mauser[6] reveals that the conversion is biphotonic, proceeding via an intermediate which is stable in the dark at 77 K. Upon monochromatic excitation at 405 nm the intermediate accumulates to an extent of up to 60%. Its absorption spectrum was obtained by deducing contributions from **4** and/or **5** according to the ratios given by the analysis[6] for various stages of the conversion. The intermediate behaves as a single, uniform species: its highly structured absorption spectrum is faithfully reproduced by the excitation spectrum of its intense fluorescence ($\tau = 190 \pm 10$ ns at 77 K) at $\lambda > 512$ nm (Figure 1). The formation of the species and its conversion into **5** upon further irradiation or to 6b,7,8,8a-tetrahydrocyclobut[*a*]acenaphthylene (**6**) upon warming above 100 K is paralleled by the buildup and decay of the characteristic ESR signals attributed[3] to the triplet state of **1**. Both ESR and optical spectra are strikingly similar to those of **3**,[5] prepared by a different photoreaction. Furthermore, a similar absorption (weak band system at $\lambda \leq 507$ nm, strong bands at $\lambda \leq 337$ nm), attributed to **2**, slowly builds up upon 365-nm irradiation of the azo compound **7** at 77 K. Apparently only a small fraction of the photochemical conversion of **7** into acenaphthene (**8**) proceeds via the stable intermediate **2** and we have not been able to accumulate sufficient quantities for a proper determination of its entire UV–vis absorption spectrum. In addition, **2** is very sensitive to light and practically nonluminescent.

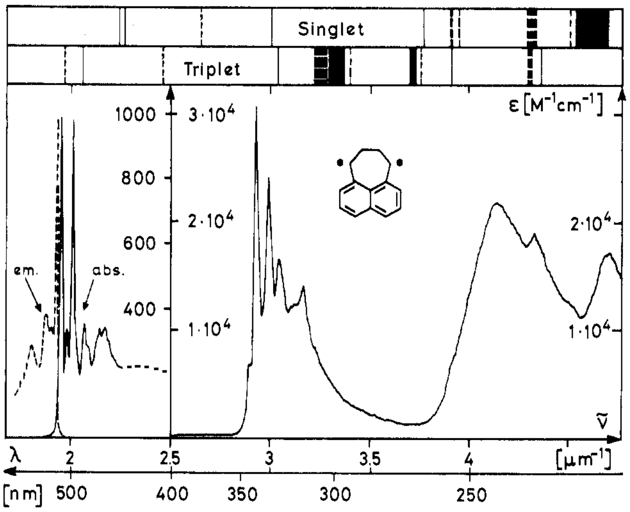

Figure 1. Absorption and emission spectrum of **1** in EPA (ether:isopentane:alcohol, 5:2:2) at 77 K. Top: electronic transitions predicted by PPP calculations for planar **2** in its lowest singlet and triplet state. Transition energies are indicated by vertical bars (full lines, transition moment parallel; broken lines, orthogonal to C_2 axis); thickness reflects calculated oscillator strength. For the singlet manifold an additional, long-wavelength transition is predicted at $0.87\ \mu m^{-1}$ (forbidden, orthogonal).

What is the multiplicity of the electronic states giving rise to the optical spectra of **1** to **3**? From ESR signal intensity variations with temperature (90–130 K for **1** and **3**, 12.5–29 K for **2**), it has been concluded that the three biradicals have a singlet ground state, the energy gap to the lowest triplet state amounting to 200 (**1**),[3] 45 (**2**),[4] and 640 (**3**)[5] cal/mol. We deduce that at 77 K the singlet/triplet ratios should be 1.3 (**1**), 0.5 (**2**), and 21 (**3**). The close similarity between the three absorption spectra is thus rather surprising, particularly since the S–S and the T–T transitions predicted by open-shell PPP SCF CI calculations[7] differ considerably (top of Figure 1) and only the triplet calculation is in satisfactory[8] agreement with experiment. Clearly inconsistent with the ESR results for **1** was the finding that both shape and intensity of its absorption were quite insensitive to a variation of the sample temperature in the range of 30–130 K. Hence, we investigated the ESR signal intensity dependence of **1** and **3** in the temperature range from 77 down to 4 K, where the thermal population of an excited triplet state should become negligible. A DPPH standard was used to check for instrumental artefacts. Relative intensities obtained from the peak to peak heights or by double integration of the derivative curves were comparable. Amazingly, the signal intensities of both **1** and **3** were nearly[9] proportional to $1/T$, as predicted by Curie's law for molecules with a triplet ground state. We may conclude that the triplet state is the electronic ground state of **1** and **3**, or lies within a few calories/mole above the lowest singlet state. If the deviations[3,5]

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