With a very efficient synthesis of **5b** via the allene **12** in hand, we have completed the synthesis of the carbon skeleton of petiodial in five steps from farnesyl bromide. Completion of the total synthesis requires adjustment of the oxidation level. Introduction of the oxygen at C(1) of **5** commenced with regioselective α-sulfenylation.[11] Minimization of γ-sulfenylation requires use of lithium *N*-cyclohexylisopropylamide as base and *S*-phenyl benzenethiosulfonate as the sulfenylating agent. Of the two γ-protons in the sulfenylation step, abstraction of the proton on the methyl group occurs selectively in spite of the doubly allylic nature of the ring methine proton. To maintain differentiation of the alcohol functions, the cyano group is transformed to an acetoxymethyl group prior to the proposed sulfoxide rearrangement[12] as outlined in Scheme I.

Use of MCPBA leads to olefin epoxidation accompanying sulfur oxidation. On the other hand, clean sulfur oxidation to the sulfoxide occurs by using the newly developed TBA-oxone.[13] The crude sulfoxide is immediately subjected to [2,3]sigmatropic rearrangement[14] to produce the desired hydroxyacetate **8**. Introduction of the final oxygen requires chemoselective hydroboration-oxidation of a 1,1-disubstituted double bond in the presence of three other double bonds. 9-BBN-H (5-fold excess) succeeds and provides a single diastereomer. To minimize steric hindrance in the approach of this bulky hydroborating agent,[15] we propose the transition state depicted in **13** which generates the relative configuration depicted in **9'**.[16] Swern-Moffatt oxidation[17] completes the synthesis. ^{1}H and ^{13}C NMR data correspond very well to the published data. Assuming no epimerization α to the aldehyde leads us to suggest the relative stereochemistry depicted in **1'** for the natural product. Since treatment of **1** with a tertiary amine leads to no change, we can only assume either that no epimerization occurs under these conditions or that any equilibrium lies heavily in favor of one diastereomer. The lack of any obvious chemical reason for the latter leads us to favor the former.

This sequence demonstrates the utility and uniqueness of the palladium-catalyzed cyclizations. The placement of the double bond in **5b** between C(7) and C(19) rather than C(7) and C(8), which does not happen in thermal Alder ene reactions, proceeds more selectively than our model system. Since we showed in the case of substrate **2** that the regioselectivity derives from the presence of the remote double bond as a binding site, the presence of two remote double bonds that might play the role of binding sites in **12** may account for the absence of any alternative isomer. The novel intervention of the allene in this cyclization demonstrates a potential for broader applicability of these metal-catalyzed cyclizations via isomerizations.

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Supplementary Material Available: Spectral data for **12**, **5b**, **8**, and **9** and a table for comparison of spectral data for natural and synthetic petiodial (2 pages). Ordering information is given on any current masthead page.

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Evidence for Extreme Activation of C-H Bonds in $[(PhCH_2)_2NNa]_n$: Resultant C-H Bond Cleavage To Give $\{[PhC(H)NC(H)Ph]Na\cdot PMDETA\}_n$

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In organolithium chemistry evidence is accumulating that lithium atoms situated in abnormally low coordination environments then proceed to interact with nearby CH units of the ligands. For example, the crystal structure of $[(PhCH_2)_2NLi]_3$ revealed a planar $(NLi)_3$ ring whose formally just two-coordinate metal atoms form close contacts with $CH_2\alpha CoCH$ portions of the benzyl groups.[1] Elsewhere, the position of second lithiation of an aromatic such as naphthalene was shown, by MO calculations on model species and by ^{6}Li-^{1}H HOESY NMR experiments, to be directed by Li···HC interactions within the monolithium species.[2] In the light of such findings we decided to explore the occurrence of like interactions in organo*sodium* derivatives: given Na's greater ionicity (so generally higher transmitted reactivity in compounds) compared to Li, one might expect any such metal···hydrocarbon interactions to be even more emphatic.

Our first target was dibenzylamidosodium, $[(PhCH_2)_2NNa]_n$, **1**, the Na analogue of the lithium amide cited above. Red crystals of compound **1** were obtained in high yield (78%) from an equimolar reaction of $(PhCH_2)_2NH$ with a suspension of Bu^{n}Na in hexane. Satisfactory elemental analyses apart, **1** was characterized through its ^{1}H NMR spectrum which showed the expected Ph and CH_2 resonances, but no resonance due to (N)*H*;[3] also relevant is that the IR spectrum of **1** clearly revealed the presence of benzyl CH_2 units [$\nu(CH_2)$, 2705-2610 cm^{-1}]. Given **1**'s low mp and reasonable solubility in hydrocarbons (e.g., 35 mg/mL in toluene) it probably has an oligomeric, rather than a polymeric, structure, e.g., a ring, akin to that found for $[(PhCH_2)_2NLi]_3$, though possibly, in view of the structure found for $(PhCH_2Na\cdot TMEDA)_4$,[4] a larger $(NNa)_n$ ring may be preferred; either way, the crux is that, in the absence of a Lewis base, a ring sodium atom in **1** would be only two-coordinate and so extremely coordinatively unsaturated.

Remarkably, treatment of **1** with the Lewis base PMDETA [$(Me_2NCH_2CH_2)_2$·NMe], or of $(PhCH_2)_2NH$ with Bu^{n}Na in the presence of PMDETA, affords needles of $\{[PhC(H)NC(H)Ph]Na\cdot PMDETA\}_n$, **2**, a dichroic material seen as green by reflected light but deep red by transmitted light. These crystals,[5] obtained in good yield (59%, first crop), are low melting, soluble in hydrocarbons (e.g., 75 mg/mL in toluene), extremely oxygen- and moisture-sensitive, and, over a longer period, light-sensitive also. Evidence for the formulation of **2**, aside from good elemental analyses, was gathered as follows. The key feature of its ^{1}H NMR spectrum, apart from the expected PMDETA and Ph resonances,

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(2) (a) Neugebauer, W.; Kos, A. J.; Schleyer, P. v. R. *J. Organomet. Chem.* **1982**, *228*, 107. (b) Neugebauer, W.; Clark, T.; Schleyer, P. v. R. *Chem. Ber.* **1983**, *116*, 3283. (c) Bauer, W.; Clark, T.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1987**, *109*, 970.

(3) Compound **1** $[(PhCH_2)_2NNa]_n$: mp 98-101 °C; Anal. ($C_{14}H_{14}NNa$) C, H, N, Na; ^{1}H NMR spectrum (recorded at 360 MHz in benzene-d_6 solution) Ph (10 H, m, centered at δ 7.16 ppm) and CH_2 (4 H, br s, δ 3.73 ppm).

(4) Schade, C.; Schleyer, P. v. R.; Dietrich, H.; Mahdi, W. *J. Am. Chem. Soc.* **1986**, *108*, 2484.

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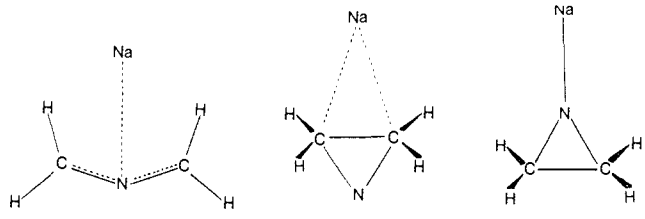
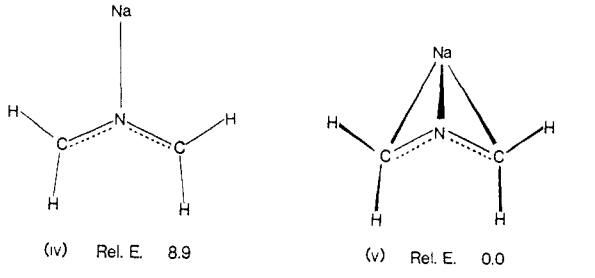
is a signal due to PhC*H* (2 H, s, δ 6.79 ppm) in lieu of one due to PhCH_2 (cf. δ 3.73 ppm for the four benzyl CH_2 protons in **1**); crucial to its assignment, this signal due to PhC*H* showed an NOE enhancement (ca. 5%) on irradiation of the *o*Ph resonance. These assignments gained from the ^{1}H NMR spectrum were supported by ^{13}C {^{1}H, broad band} and ^{13}C DEPT NMR experiments which located the distinct C atoms of PMDETA, Ph, and PhC*H*.[5] Equally significant, the IR spectrum of **2** reveals no $\nu(CH_2)$ absorptions in the range 2750–2600 cm^{-1} (cf. **1**'s IR spectrum); however, a very strong band at 1580 cm^{-1}, not present in the spectrum of **1**, appears, assignable in this system to either C=N or C⋯N⋯C groups.

The above accumulated evidence shows that $[(PhCH_2)_2NNa]_n$, **1**, converts into the complex, {[PhC(H)NC(H)Ph]Na·PMDETA}$_n$, **2**, on treatment with PMDETA. In the absence of a crystal structure for **2** (which in view of **2**'s acute sensitivity may not be forthcoming), we have performed ab initio MO geometry optimizations[6] of several possible model (uncomplexed, monomeric)[7] structures, with H substituted for Ph: these {[HC(H)NC(H)H]Na} structures, determined by using 6-31G/66-31G basis sets, are shown in i–v, with their relative energies (kcal/mol) indicated.





The planar Na–aza–allyl arrangement i and the fused-ring system ii are clearly energetically unfavorable and thus can be dismissed. Model iii, the N-substituted aziridine ring, in concert with its acyclic analogue iv would, with tridentate PMDETA incorporated, provide Na with a formal coordination of 4. However, model v, another aza–allyl species but one with a Na position (77.1° out of the C⋯N⋯C plane) that facilitates both N–Na (2.307 Å) and C–Na (2.538 Å) [cf. 2.64/2.76 Å for the C–Na bonds in the aforesaid $(PhCH_2Na\cdot TMEDA)_4$[4]] interactions, is the most stable. An additional feature of model v is that the two H atoms attached to each C are also tilted away from the CNC plane, though to the opposite side from Na, at angles of 7° and 11°. It is reassuring to note that model v can rationalize the absorption at 1580 cm^{-1} in **2**'s IR spectrum (i.e., as the two C⋯N bonds are found to be 1.319 Å long, with an associated bond order of 1.59; the CNC bond angle is 125.7°).

This favored structure in effect, on incorporation of PMDETA,[8] provides Na with a high coordination number (of 6, cf. probably 2 in **1**). In addition, the $(PhCH)_2N^-$ anion in **2** is presumably stabilized somewhat, by delocalization (feasible over its entire length), relative to the $(PhCH_2)_2N^-$ anion in **1**. However, this latter contribution would of course pertain irrespective of the metal: yet, on treatment with Lewis bases, $[(PhCH_2)_2NLi]_3$ forms simple complexes in which the dibenzylamido units remain intact.[1] The implication is that the metal···H_2C interactions apparent in $[(PhCH_2)_2NLi]_3$ are much more dramatic when the metal is Na, i.e., in **1** which will have even greater ionic character: so dramatic, in fact, that they lead to actual *cleavage* of one of the C–H bonds in each benzyl CH_2 unit. How this *formal* H_2 elimination occurs is as yet unknown. However, no sign of gas evolution is observed during reaction of **1** with PMDETA; this, plus the fact that **1** itself does not spontaneously rearrange (i.e., PMDETA addition is required), suggests that H^+-transfer from weakened C–H bonds in **1** to PMDETA plays a role.

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(5) Compound **2** {[PhC(H)NC(H)Ph]Na·PMDETA}$_n$: mp 167 °C; Anal. ($C_{23}H_{35}N_4Na$) C, H, N, Na; ^{1}H NMR spectrum (25 °C) (recorded at 360 MHz in tetrahydrofuran-d_8 solution) PMDETA [(Me_2N)$_2$, 12 H, s, δ 2.31 ppm; *Me*N, 3 H, s, δ 2.24 ppm; (CH_2CH_2)$_2$, 8 H, d of m's, centered δ 2.45 and δ 2.53 ppm], Ph (*o*, 4 H, br s, δ 7.04 ppm; *m*, 4 H, m, centered δ 6.95 ppm; *p*, 2 H, m, centered δ 6.34 ppm), and PhC*H* (2 H, s, δ 6.79 ppm); ^{13}C NMR (25 °C) (recorded at 90.6 MHz in tetrahydrofuran-d_8 solution) PMDETA [(Me_2N)$_2$, δ 44.76 ppm; (*Me*N), δ 41.94 ppm; (CH_2CH_2)$_2$, δ 55.48/57.42 ppm], Ph (*p*, δ 110.06 ppm; *o*, δ 117.50 ppm; *m*, δ 127.91 ppm; ipso, δ 144.27), and PhCH (δ 114.35 ppm).

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(7) Cryoscopic relative molecular mass (CRMM) measurements show that **2** is monomeric in benzene solution at a concentration of 0.014 M, CRMM = 395 ± 20, n = 1.01 ± 0.05.

(8) Calculations have also been carried out on [HC(H)NC(H)H]Na·OH_2 in order to evaluate the effect of complexation on the geometry of model v. It is found that the presence of H_2O does not alter the gross geometrical features of v; thus Na is positioned above the aza–allyl unit at an angle of 82°, with N–Na and C–Na bond lengths of 2.329 and 2.610 Å, respectively.