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Metal-Induced Reductive Cleavage Reactions: An Experimental and Theoretical (MNDO) Study on the Stereochemical Puzzle of Birch and Vinylogous Birch Processes

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The stereochemical puzzle posed by the lithium-promoted Birch and vinylogous Birch reductive cleavage of unsaturated benzyl ethers (BICLE; takes place with retention of configuration of the sensitive $^2\Delta$ double bond) and the corresponding cinnamyl analogs (VIBICLE; gives rise to ca. 2.5:1 *E*:*Z* mixtures) has been approached by experimental and theoretical means. NMR experiments indicate that the π-type organolithium compounds resulting from these reactions do not form observable mixed aggregates with the lithium silyloxide species generated alongside in the reaction and do not undergo observable isomerization at the temperature of operation. A simplified model for contact, solvent-separated, and isolated ion pairs has allowed us to evaluate these complex reactions in great detail from a theoretical viewpoint, using the MNDO semiempirical method. Relevant features that come out from these comprehensive studies, for which we have employed lithium naphthalenide (LiNaph) or lithium benzenide (LiBenz) as promoters, are as follows: (1) the lowest energy routes for cleavage are those involving contact ion pairs (CIPs) in which the lithium counterion plays a key role by acting as a handle (Lewis acid) to which the leaving group $^-$OR adheres prior to detachment; (2) the different haptomeric structures which reside (local minima) in the potential hypersurface of either the so-called radical anion or the dianion routes show that haptomeric activation is key to understanding cleavage of the C−O bond which, eventually, takes place as a syn β elimination of LiOR; and (3) reductive cleavage of unsaturated benzyl ethers (BICLE) involves transient cation/anion radicals which undergo cleavage and subsequent reduction to the final organolithium with retention of configuration, in accordance with experiment, whereas that of vinylogous cinnamyl ethers (VIBICLE) involve transient dianion/dication species resulting from long-lived cation/anion radicals. In good qualitative agreement with experiment, MNDO finds two diastereomeric routes ($\Delta\Delta G^* = 0.2$ kcal/mol) for cleavage of (appropriately substituted) cinnamyl ethers, but only one for cleavage of the unsaturated benzyl analogs.

Introduction

The metal-induced reductive cleavage of benzylic ethers and related compounds[1] is commonly used in preparative synthetic organic chemistry.[2] Nonetheless, both the detailed mechanism[3] and the actual structure of the final species thereby generated, i.e., in the case of a lithium-promoted reaction, an organolithium compound together with a lithium salt (alkoxide, sulfide, halide, or other), are largely ignored at present.[4] In a recent study aimed at the stereocontrolled synthesis of prenylated quinones and aromatics, we used the so-called vinylogous Birch hydrogenolysis (VIBIHY) of cinnamyl silyl ethers as well as the Birch hydrogenolysis (BIHY) of the corresponding unsaturated benzyl silyl ethers as the key steps for the $^2\Delta$ stereocontrolled introduction of prenyl chains into aromatics.[5] In this study, we uncovered a previously unnoticed observation, namely that vinylogous Birch hydrogenolysis of cinnamyl alcohols (as silyl ethers) rendered the expected isoprenyl chains as $^2\Delta$ *E*,*Z* mixtures (ca. 2.5:1), whereas Birch hydrogenolysis of the corresponding *E* or *Z* unsaturated benzyl alcohols (also

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(8) The radical anion/cation and dianion/dication nomenclature is used throughout for clarity. By dianion/dication we mean to describe not only plain ion pairs but also triple ion species (i.e., cation/dianion/cation) presumably resulting from reactions that employ alkali metals (with or without a carrier) as reductants.

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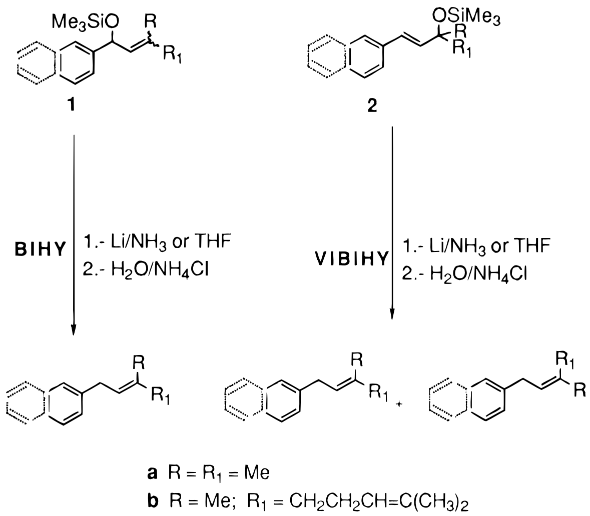
Scheme 1



as silyl ethers) takes place instead in a highly stereocontrolled manner, i.e. with complete retention of configuration of the sensitive $^{2}\Delta$ double bond,[2e–i, 5] thereby providing a unique entry to prenylated systems (Scheme 1).[5–7]

This puzzling stereochemical behavior could be thermodynamic in nature and operate either after or before cleavage (Figure 1). The former possibility (i.e., after cleavage) required that either the radicals (if cleavage were to occur from a radical anion/cation species[8]) or the organolithium compounds (if cleavage were to take place at the dianion/dication stage[8]) resulting from BICLE and VIBICLE were structurally different species so that only one could undergo equilibration. Assuming, in principle, that a common mechanism would operate for both reactions, the above condition would certainly not be attended for simple radicals or organolithium species, but it could be met if complexation with the coexisting lithium salts in solution were possible, a chance that we could envisage for the final organolithium compounds (see below). The later possibility (i.e., thermodynamic equilibration prior to cleavage) required BICLE and VIBICLE to give rise to intermediate species having well-differentiated lifetimes so as to allow for equilibration in one case but not in the other.[9] On the other hand, the observed results might well be entirely kinetic in nature, thereby implying that a bias should be available for the vinylogous series only. Alternatively, BICLE and VIBICLE reactions might just involve different reaction mechanisms. In trying to find appropriate explanations to the above intriguing problems, we decided to address, from experimental and theoretical viewpoints, the following two main objectives: (1) the structure and (stereochemical) properties of the final organometallic species present in solution and (2) the mechanistic details of the lithium-promoted Birch (BICLE) and vinylogous Birch cleavage (VIBICLE). By so doing, we aimed at reaching the goal of providing a full picture of metal-promoted reductive cleavages in which the role of counterion and solvent effects would be, at least in part, examined.

Central to the first objective was the question of whether or not a π-type organolithium compound would form a "unimetal superbase"[10] by interacting with the lithium alkoxide being generated alongside in the reaction.[4,11] Were this the case, we conceived the idea that the above stereochemical issue could be the consequence of some poorly understood equilibrating process accessible for the mixed species derived from cinnamyl ethers but not for those resulting from the isomeric unsaturated benzyl ethers.[12] Accordingly, we decided to examine the solution structure[4a,13] and stereochemical properties of the organolithium species resulting from BICLE and VIBICLE processes by means of NMR spectroscopy of the magnetic nuclei (^{1}H, ^{13}C, ^{6}Li, and/or ^{7}Li) available.[14] In addition, we planned to carry out a quantum (MNDO) chemical study which would allow us to deal with hapticity, a structural property of π organolithium compounds that we deemed of considerable significance for understanding the stereochemical issues posed by metal-promoted reductive cleavage (see below). It is worth mentioning in this regard that benzyllithium actually crystallizes out as different haptomeric structures depending on the solvent and ligands present during its generation,[15] thereby showing that lithium haptomers (and lithium tropomers[16]) might be separated by just a few kcal/mol and, accordingly, that the equilibria involving these species may be displaced toward one side or another by modifying such operational variables as solvent, temperature, or concentration.[17]

Our second objective called for carrying out a theoretical study of BICLE and VIBICLE processes in order to assess the likely role of the counterion[18] and solvent both

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(10) Caubère, P. *Chem Rev.* **1993**, *93*, 2317 and references therein. For some recent monographs on "complex bases" or "super bases", see also: Schlosser, M. *Pure Appl. Chem.* **1988**, *60*, 1627. Mordini, A. In *Advances in Carbanion Chemistry*; Snieckus, V., Ed.; JAI Press; Greenwich, CT, 1992. Multimetal superbases are also the matter of current interest and controversy. See, for example: Bauer, W.; Lochman, L. *J. Am. Chem. Soc.* **1992**, *114*, 7482.

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(12) For a recent review on polar allyl-type organometallics, see: Schlosser, M.; Desponds, O.; Lehmann, R.; Moret, E.; Rauchswalbe, G. *Tetrahedron* **1993**, *49*, 10203.

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(14) For a recent review on the NMR structural investigation of organolithium compounds, see: Bauer, W.; Schleyer, P. v. R. In *Advances in Carbanion Chemistry*; Snieckus, V., Ed.; JAI Press; Greenwich, CT, 1992; Vol. 1.

(15) Benzyllithium X-ray structures: (a) Patterman, S. P.; Karle, I. L.; Shicky, G. D. *J. Am. Chem. Soc.* **1970**, *92*, 1150. (b) Beno, M. A.; Hope, H.; Olmstead, M. M.; Power, P. P. *Organometallics* **1985**, *4*, 2117. (c) Zarges, W.; Marsch, M.; Harms, K.; Boche, G. *Chem. Ber.* **1989**, *122*, 2303. For some theoretical studies on the structure of benzyllithium, see: (d) Lipkowitz, K. B.; Uhegbu, C.; Naylor, A. M.; Vance, R. *J. Comput. Chem.* **1985**, *6*, 62. (e) Sygula, A.; Rabideau, P. W. *J. Am. Chem. Soc.* **1992**, *114*, 821.

(16) For an example in which lithiotropicity has been observed in the solid state, see: Boche, G.; Etzrodt, H.; Massa, W. Baum, G. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 863.

(17) (a) Schleyer, P. v. R. *Pure Appl. Chem.* **1983**, *55*, 355. (b) Schleyer, P. v. R. *Pure Appl. Chem.* **1984**, *56*, 151. (c) Streitwieser, A., Jr. *Acc. Chem. Res.* **1984**, *17*, 353.

(18) Counterion-free "carbanions" are more a pedagogic aid than really abundant chemical species. See: Lambert, C.; Schleyer, P. v. R. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1129.

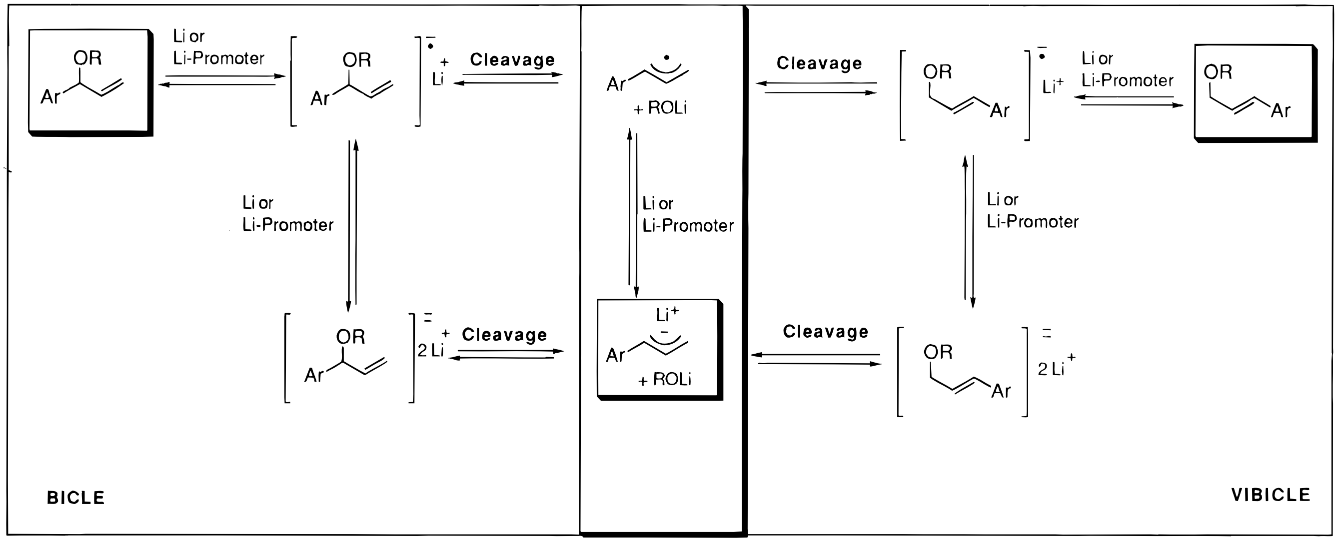

Figure 1. Alternative routes for BICLE and VIBICLE cleavage. Common intermediates and/or products in boxes.

in cleavage and stereochemistry. To this end, we have carried out calculations for radical anion/cation and dianion/dication species in the following three limiting situations: (a) with discrete counterion solvation as a model for reactions involving contact ion pairs;[19] (b) in a solvent continuum (nonintervening counterions are considered apart for thermodynamic purposes) as a very simplified model for solvent-separated ion pairs;[20] and (c) counterion-free species in vacuo as model for cleavage reactions promoted by electron transfer (from a metal or otherwise) which, presumably, involve counterion-free species.[9,21] By so doing, we expected to be able to assess the relative importance of some of the myriad equilibria involved in reductive cleavage reactions and determine the role of the counterion that we envisaged, at the outset, responsible for cleavage.

Reductive cleavage reactions promoted by electron transfer encompass two fundamental operations irrespective of the number of electrons involved, according to the unifying mechanistic pattern generally accepted.[3] First, the unsaturated group (if any) of the substrate acts as a (temporary) captor during the primary act of electron transfer. Presumably, electrons act as "messengers" by migrating intramolecularly to a σ moiety of the substrate which is thus activated toward its eventual dissociation because the σ^* state becomes partially populated.[22] Both operations (electron transfer and cleavage) can either be concerted or stepwise, thus giving rise to the standard set of alternative mechanistic routes.[3,21] Likely, as pointed out by Bock and co-workers,[23] the mechanistic picture is that of a multidimensional network equilibria actually interconnecting electron transfer, ion pair solvation, and aggregation processes in which the metal intervenes decisively. However, until recently, the role assigned to the metal in metal-promoted processes was merely that of acting as the electron source but none in the rate-determining cleavage step. In particular, counterion-free radical anions have been usually invoked as key intermediates in the alkali metal-promoted reductive cleavage of ethers[1a,3] (diaryl and alkylaryl ethers), alkyl halides,[24] and sulfides,[1d,25] mostly on the basis of product studies.[26] Moreover, according to the principle of regioconservation of spin density due to Maslak and Guthrie,[27] the regioselectivity of the α cleavage undergone by anion radicals (whether long or short lived) derived from alkylaryl and diaryl ethers should occur so that the unpaired electron remains on the same side of the scissible bond. However, even the regiochemical issue is far from being definitely settled as new, controversial results, stereochemical or otherwise, continue to appear.[28] Remarkably, no attention has been paid in these studies to the possible role played by the metal center in the cleavage of radical anions, in spite of the well-known effect of the metal on the hyperfine coupling observed in

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[19] Szwarc, M.*Ions and Ion-Pairs in Organic Reactions*; Wiley-Interscience: New York, 1972; Vol. 1.

[20] The structure of solvent-separated ion pairs is much more dynamic than that of contact ion pairs, the distance between ions being no less than 7 Å. See: Weller, A. Z. *Phys. Chem.* **1982**, *130*, 129. Our choice of a model for SSIP's, though static, mets two of these criteria, namely: (1) there is no interaction between ions, and (2) they are strongly solvated by the medium.

[21] Electrochemically-induced reductive cleavage reactions are ususally written as involving counterion-free species. See, for example: (a) Savéant, J.-M. *Tetrahedron* **1994**, *34*, 10117. (b) Savéant, J.-M. *Adv. Phys. Org. Chem.* **1990**, *26*, 1. (c) Bunnett, J. F. *Acc. Chem. Res.* **1978**, *11*, 413.

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the ESR spectra of radical anion/cation species.[29] Only a recently published investigation claimed, on the basis of experimental (ESR, ENDOR, and triple studies) and low-level theoretical (Hückel and INDO) calculations, that the counterion actually determines the lowest energy conformation of the radical anion/cation pair.[30] Furthermore, even though solvation, concentration, and temperature are known to affect the structure of the radical anion salts (ketyls) resulting from metal reduction of aromatic ketones,[31] counterion and solvation effects in redox reactions remain "sunk at unknown depths",[32] especially for those processes which involve two electron transfer steps with concomitant cleavage of a C−X bond in a position α or β to an existing π system.[33]

Much more information is available for electrochemically-induced reductive cleavage reactions which are known to take place in a thin reaction layer on the electrode surface.[9g] Savéant's cyclic voltammetric studies call for two mechanistic scenarios according to the concerted or stepwise nature of single electron transfer and cleavage.[21] In the inner sphere process, both are concerted whereas in the outer sphere process electron transfer and cleavage are consecutive steps involving an intermediate radical anion. The electrochemical reduction of alkyl halides,[9b] benzyl halides,[9a] aryl halides[9d] and *N*-halosultams[9f] appears to conform to this dual mechanim, claims to solvent[9a] and counterion effects being only made to account for the strikingly different kinetic behavior of the otherwise identical radical anion species resulting from electrochemical or radiolysis processes.[9f]

The scenario for our studies was still somewhat broader as, in principle, the rate-determining cleavage step of BICLE and VIBICLE processes (Figure 1) might involve not only the so-called radical anion but also the dianion species (actually radical anion/cation and/or dianion/dication pairs).[34] Walsh has provided kinetic evidence for the simultaneous occurrence of cleavage (of a carbon−carbon bond) mechanisms from the radical anion and dianion intermediates,[35] the later species resulting from disproportionation[36] or reduction of the corresponding radical anion.[34] Other examples from the old and recent literature[37] claim that cleavage occurs from dianions, though to the best of our knowledge, only Kiesele[38] has been able to demonstrate that the counterion plays a key role, however unespecified, in the rearrangement reaction following cleavage. Curiously enough, despite the fact that dianions been have also invoked by numerous workers in the past, this mechanism is not unfrequently quoted as "unnecessary".[1a,34]

Irrespective of whether cleavage involves a radical anion/cation or dianion/dication species, we hypothesized that lithium ought to play a key role in promoting cleavage in BICLE and VIBICLE processes by acting as an internal Lewis acid in assisting the departure of the leaving group and thus perhaps provide a bias for stereochemical discrimination. In addition, we contended that the metal atom should also be responsible for the "messenger" role in activating positions far away from the electron sink because of the likely shallow nature of the potential energy surface of π organolithium species.[39] Herein, we show that BICLE and VIBICLE are both stepwise processes, each giving rise to π-type organolithium species which do not undergo appreciable equilibration at $T < 0$ °C. However, as shown below by calculations, a fundamental difference exists between them: BICLE processes involve transient radical anion/cation intermediates whereas VIBICLE reactions give rise to radical anion/cation intermediates that can accumulate as they are more stable (either as contact ion pairs, CIPs, or solvent separated ion pairs, SSIPs[19]) than starting materials and, hence, undergo conformational (but not configurational, see below) equilibration prior to cleavage. Actually, according to MNDO, the stereochemical outcome of VIBICLE reactions appears to be due to the combination of two factors: (a) cleavage in the vinylogous series involves the dianion/dication species, and (b) the styryl unit can (if appropriately substituted) function as a chiral plane, thereby giving rise to two competitive, diastereoisomeric routes for cleavage.

Computational Methods

For this study we have used the MNDO semiempirical treatment for which lithium has been parametrized.[40] MNDO, in spite of its well-known shortcomings,[41] has proven to be reliable for studying the very large structures of organolithium compounds as contact ion pairs,

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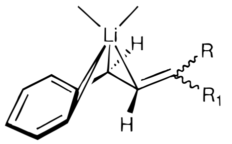
their predictions being, in many cases, in close agreement with experimental data resulting from X ray and/or spectroscopic studies.[42]

For CIPs, calculations have been performed using discrete solvation[43] of lithium with two NH_3 molecules (per lithium) as working model.[44] Calculations "in vacuo" or in a "dielectric continuum" (COSMO)[45] have been used to modelize isolated, nonsolvated ion pairs (IIPs)[46] and the corresponding solvent separated ion pairs (SSIPs), respectively.[19] No geometrical constraints were imposed except for the case of cinnamyl derivatives for which the π system was kept planar throughout. Due to MNDO's overestimation of steric repulsions, the corresponding nonplanar structures were found to be somewhat lower in energy. All structures were optimized and further refined by minimization of the gradient norm at least below 0.1 kcal/Å·deg. All stationary points on the potential energy surfaces were characterized by calculating and diagonalizing the Hessian matrix and by checking the number of negative eigenvalues.[47] All ΔG values refer to 273 K.

Discussion

Experimental Studies. Experiments were set so as to learn if the final π organolithium compounds would form mixed aggregates with the coexisting lithium salts. The structure of the organolithium species **3ia** (Figure 2) generated by treatment of silyl ethers **1a** and **2a** with ^{6}Li in dried THF-d_8,[5] at 0 °C for 1 h, could be gleaned from its NMR spectra.[5] In both BIHY and VIBIHY cases, the ^{6}Li spectra showed two different signals at 2.18 and 3.03 ppm, presumably corresponding to a single organolithium compound concurrent with lithium trimethylsilyl oxide. The ^{1}H and ^{13}C NMR spectra which were found to be similar to those already published for other phenylallyllithium compounds also confirmed this initial assignment.[48] Relevant to our first objective, we found that both the organolithium compound and the lithium silyloxide species in solution did not interact with each other as evidenced by the ^{6}Li−^{1}H HOESY[49] spectrum (supporting information) for which the phase cycle reported by Bauer[50] gave best results. Thus, the lithium at 3.03 ppm correlated with the methyl groups of the Me_3-Si group only, whereas that at 2.18 ppm gave a large cross peak with the benzylic hydrogen (3.66 ppm), two small ones with the vinylic hydrogen (6.06 ppm), and an aromatic ortho hydrogen (5.86 ppm) and a very small one with the methyl group (1.58 ppm) syn to the benzylic hydrogen. Altogether, these features clearly define the following structural picture: (1) the solution structure of the organolithium compound **3ia** (Figure 2) generated by both BICLE and VIBICLE processes is that of a vinyl substituted η^3 benzyl lithium,[51] thereby suggesting a reasonable explanation for the regioselectivity of the protonation step;[52] and (2) the organolithium compound and the lithium (trimethylsilyl) oxide (or derivative thereof) present in solution do not interact with each other as shown by the absence of cross peaks in the ^{6}Li−^{1}H HOESY spectra and lithium−lithium interactions in the bidimensional ^{6}Li−^{6}Li INADEQUATE[53] spectra.[54] This structural analysis is, at least, valid for the −50 to 25 °C range for which no significant modifications on the above spectra were observed, except for some sharpening of the lithium silyloxide signal at 3.03 ppm. At temperatures above 40 °C, quenching of the organolithium species took place. The possible existence of mixed species in very low equilibrium concentration cannot, however, be discarded from the available data (see below for quantum chemical results).



3ia R = R_1 = Me

3ib R = Me; R_1 = $CH_2CH_2CH{=}C(CH_3)_2$

3ic R = H; R_1 = Me

3id R = R_1 = H

Figure 2.

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The results of an analogous NMR study on the BICLE and VIBICLE reactions undergone by (*E*)-**1b**, (*Z*)-**1b** and (*E*)-**2b** clearly demonstrated that isomerization of the final organolithium species (*E*)-**3ib** and (*Z*)-**3ib** (Figure 2) is extremely slow at the temperature of operation (−20 °C), thus proving that the puzzling stereochemistry observed must be settled in previous steps. Actually, analysis of the ^1H and ^{13}C NMR spectra as well as $^6Li-^1H$ HOESY of the red solutions of organolithium compounds (*E*)-**3ib** and (*Z*)-**3ib** resulting from (*E*)-**1b** (95% stereochemically pure) and (*Z*)-**1b** (92% stereochemically pure), respectively, attested to the fact that BICLE processes had occurred with retention of configuration of the sensitive $^2\Delta$ double bond, the observed *E*:*Z* ratio for (*E*)-**3ib** (95:5) and (*Z*)-**3ib** (8:92) not being modified by standing at −20 °C for 24 h. Isomerization is fast (a ca. 2.5:1 *E*:*Z* mixture is obtained after 30 min) at a higher temperature (27 °C).[48b] The VIBICLE process carried out with pure (*E*)-**2b** yielded,[5] instead, a ca. 2.5:1 mixture of *E* and *Z* organolithium species as determined by integration of benzylic (δ 3.63 and 3.76 ppm) signals, respectively. This ratio did not suffer alteration after being allowed to stand for 24 h at 25 °C.

MNDO Studies. As neither the final organolithium nor the corresponding protonated material isomerized at the temperature of operation,[55] we were left with the "dark" part of the mechanism to explain the stereochemical questions posed by BICLE and VIBICLE processes. Accordingly, we headed for a detailed theoretical study[46] of the above ether cleavage reactions as applied to α-vinylbenzyl methyl ether **4** and the corresponding cinnamyl methyl ether **11**, our models for BICLE (Scheme 2) and VIBICLE processes (Scheme 3), respectively. As mentioned above, the most relevant parts of this broad plan included the study of the following: (1) reactions involving contact ion pairs (CIP's are labeled throughout with the appropriate numerals and a subscript (i or ii) indicating the number of lithium atoms) which we modeled as organolithium species having discrete solvation (two ammonia ligands per lithium) around the counterion; (2) reactions involving solvent-separated ion pairs (SSIP's; labeled with a numeral with the appropriate (i) or (ii) subscripts) which we modeled by using noninteracting ions solvated by the "dielectric continuum" provided by COSMO;[47] and (3) reactions involving isolated, nonsolvated ion pairs (IIP's; labeled throughout the work by numerals, only).

As processes involving electron transfer from metals to organic substrates are not amenable to semiempirical calculations because neither kinetic nor thermodynamic reliable data can be easily obtained,[56] we focused, instead, our attention on lithium naphthalenide-promoted reactions (either as LiNaph$^\bullet$, $Li^+_{(solv)}||Naph^{-\bullet}_{(solv)}$ or Li^+ $Naph^{-\bullet}$) to circumvent the problem. Closely related lithium benzenide has also been employed in our calculations as a model for the well-known mediator lithium di-*tert*-butyl biphenylide (LiDBB).[57] The only kinetic stages that escaped from this analysis were, obviously, those of electron transfer since the TS for these processes cannot be found.[56] For the sake of discussion a clear-cut distinction is made between the reduction and cleavage steps.

The Reduction Step: Activation for Cleavage. The role of the media and that played by the metal during reduction of different substrates can be scrutinized from the following thermodynamic data. One-electron reduction of **4** (BIHY) or **11** (VIBIHY) gives rise to radical anions **5** or **12**, respectively, but to radical anion/cation pairs either as CIP's (**5i** and **12i**) or SSIP's (**5(i)** and **12(i)**). Particularly meaningful to our stereochemical questions is the finding that reduction of **4** with lithium naphthalenide is a clear-cut thermodynamically uphill process (**4** → **5i**, $\Delta G = +2.9$ kcal/mol; **4** → **5(i)**, $\Delta G = +7.6$ kcal/mol; **4** → **5** $\Delta G = +9.2$ kcal/mol), whereas that of the vinylogous system **11** is slightly downhill for CIP's only (**11** → **12i**, $\Delta G = -2.8$ kcal/mol; **11** → **12(i)**, $\Delta G = +0.4$ kcal/mol; **11** → **12**, $\Delta G = +0.3$ kcal/mol). As expected, subsequent reduction to the corresponding dianion/dication species was found to be endothermic in all cases for both BICLE (**4** → **9ii**, $\Delta G = 20.4$ kcal/mol; **4** → **9(ii)**, $\Delta G = 36$ kcal/mol; **4** → **9**, $\Delta G = 141.3$ kcal/mol)) and VIBICLE (**11** → **16ii**, $\Delta G = 3.2$ kcal/mol; **11** → **16(ii)**, $\Delta G = 10.6$ kcal/mol; **11** → **16**, $\Delta G = 108.9$ kcal/mol) processes.[58] Calculations using LiBenz in place of LiNaph (supporting information) head in the same direction as

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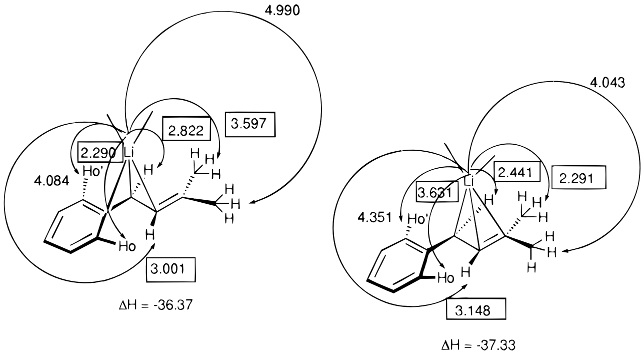
(51) The MNDO-determined structure for **3ia** accounts reasonably well for the spectroscopic data obtained as only those hydrogens located at <3.5 Å should give cross peaks with lithium in $^6Li-^1H$ HOESY spectra. A rapid equilibrium between the haptomeric structures shown below (geometric parameters relevant to $^7Li-^1H$ HOESY experiments in boxes). cannot be discarded with the available NMR data. MNDO calculations reveal that these haptomeric structures are separated by only 1 kcal/mol.



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(54) Curiously enough, benzyl methyl ether itself when submitted to the typical reaction conditions (^6Li, THF-d_8, 0 °C, sonication) showed only one lithium atom in the ^6Li NMR spectra, namely that corresponding to benzyllithium. Lithium methoxide was apparently absent (no hydrogen or lithium signals in the ^1H and ^6Li NMR spectra), thus proving that lithium methoxide prefers to aggregate rather than form a mixed complex with a π-type organolithium species. Actually, lithium methoxide is seen as a suspension in the NMR tube.

(55) The final isoprenylated aromatics did not suffer isomerization under the usual[5] reaction conditions (lithium in liquid ammonia),[55a] as demonstrated by quenching the deep blue solution resulting from lithium/liquid ammonia cleavage of (*E*)-**1b** or **(***E***)-2b** with Fe(III) and stirring the colorless solution (containing lithium amide) for several hours at room temperature. The standard workup furnished the same results as for the regular case.[5] In other words, lithium amide did not induce significant isomerization of the prenylated aromatics at the temperature of operation.[55b] (a) Rabideau, P. W. *Tetrahedron* **1989**, *45*, 1579. Rabideau, P. W.; Marcinow, Z. In *Organic Reactions*; John Wiley & Sons: New York, 1992; Vol. 42. (b) Rabideau, P. W.; Huser, D. L. *J. Org. Chem.* **1983**, *48*, 4266.

(56) AM1 has been reported to behave well in a simple test case, namely the self-exchange electron transfer reactions between a neutral aromatic and the corresponding cation radical. See: Rauhut, G.; Clark, T. *J. Am. Chem. Soc.* **1993**, *115*, 9127.

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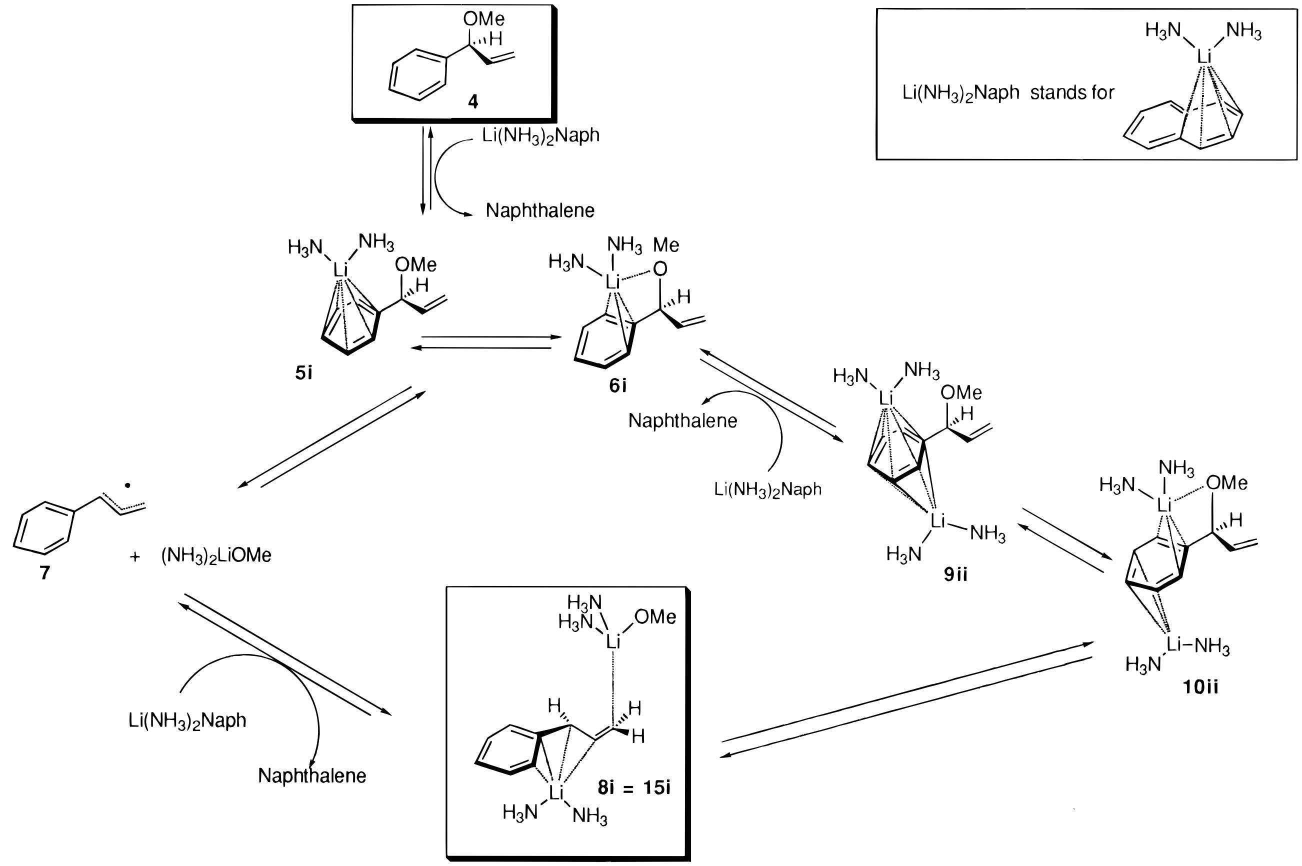
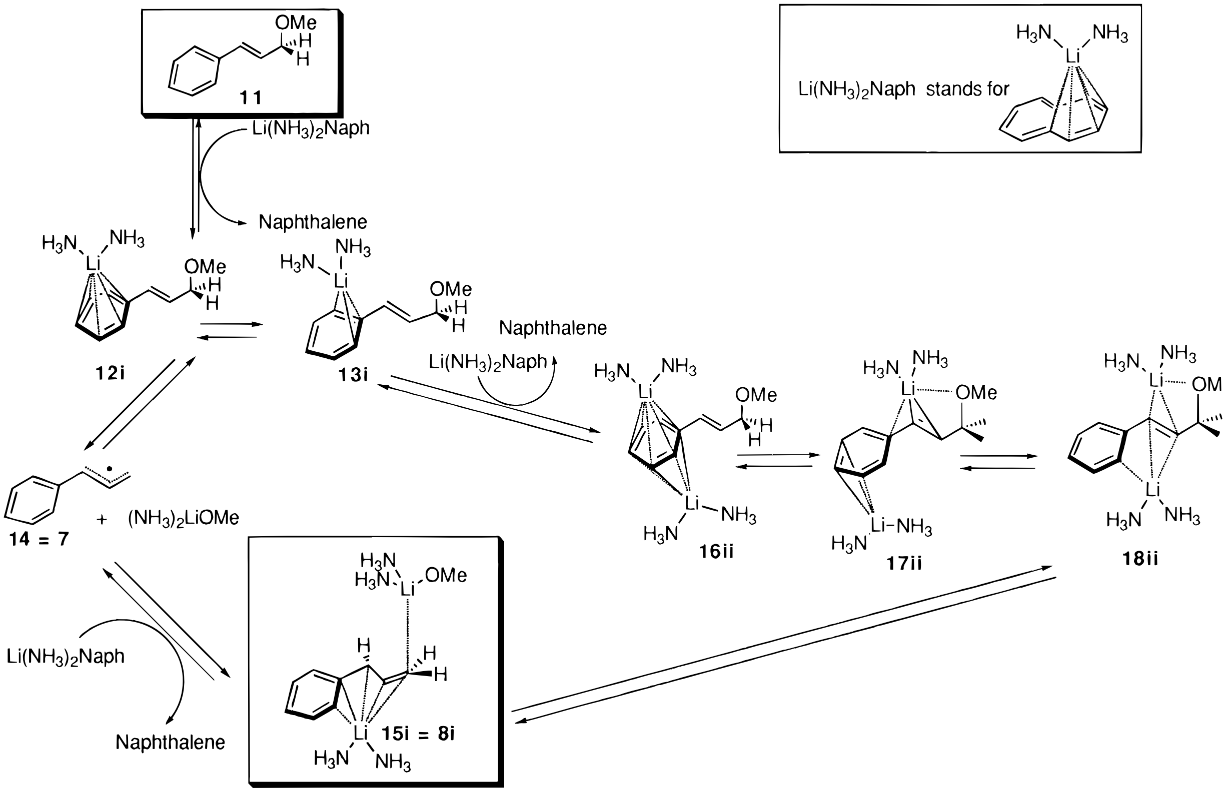
(58) *Ab initio* calculations revealed that the formal reaction $C_6H_6 + 2Li \rightarrow C_6H_6Li_2$ is endothermic by 13.4 kcal/mol. See: Sygula, A.; Rabideau, P. W. *J. Am. Chem. Soc.* **1991**, *113*, 7797.

Scheme 2. Alternatives Routes for Birch Reductive Cleavage of Benzyl Ether 4 Promoted by Lithium Naphthalenide



Scheme 3. Alternatives Routes for Vinylogous Birch Reductive Cleavage of Cinnamyl Ether 11 Promoted by Lithium Naphthalenide



illustrated by the finding that $\Delta G = +3.5$ kcal/mol for the BICLE process (**4** + LiBenz → **5i**) but -1.5 kcal/mol for the VIBICLE (**11** + LiBenz → **12i**) tranformation. In principle, a plausible explanation for the stereochemical dilemma posed by BICLE and VIBICLE could be built on these grounds as only VIBICLE processes can lead to

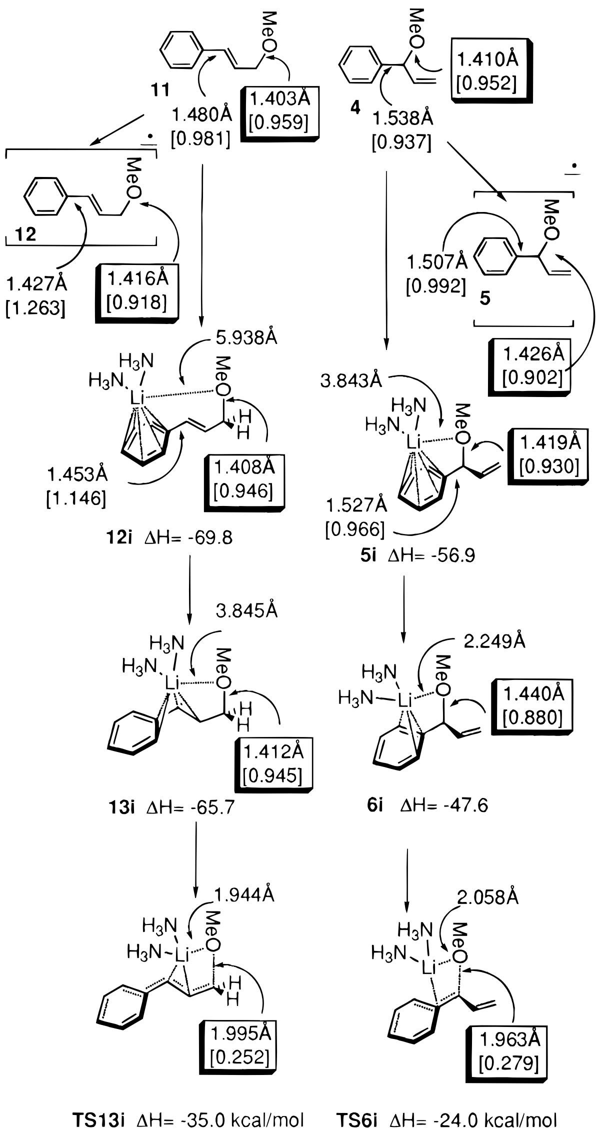


Figure 3. MNDO-determined structures of intermediates and transition states for the cleavage of benzyl and cinnamyl ethers **4** and **11** through anion-radical routes involving CIP's and IIP's (SSIP's species not shown). Geometrical features relevant to haptomeric activation are shown: (1) C−OMe bond length and bond order (in brackets); 2) Li−OMe distance; and (3) enthalpy of formation.

an intermediate radical anion/cation (as a CIP species) that can accumulate and, therefore, undergo isomerization. However, the considerable double bond character (1.359 Å, [1.718]) retained by C_2-C_3 in **12i** (or haptomers thereof; see below) clearly militates against *E*/*Z* isomerization at this point of the reaction coordinate, as it would be too energy costly. Thus, we decided to study cleavage from the so-called radical anion and dianion species (either as IIP's, CIP's, and SSIP's) derived from Birch and vinylogous Birch reactions.

A number of mechanistically meaningful features result after one-electron reduction of **4** or **11** (Figure 3), the most relevant being that the C−O bond becomes fixed in a partially locked conformation. For the most part, this is a consequence of the fact that the key C−O bond tries to become parallel (syn or anti) to the π system (dihedral angle = 59.8°, for the syn species) to facilitate overlap and also marginally due to the interaction between lithium and the oxygen atom. Accordingly, rotation around the C_{ipso}−CHROMe bond in radical anion/cation **5i** is partially restricted as illustrated by the fact that this bond is somewhat shortened in going from **4** (1.538 Å) to **5i** (1.527 Å). Interestingly, this is irrespective of the presence or absence of counterion (according to our modelization for SSIPs, their geometrical features are almost indistinguishable to those of the corresponding IIPs). Actually, the counterion-free radical anion **5** shows an even shorter C_{ipso}−C bond (1.507 Å), and activation of the C-O bond (1.426 Å) is stronger than in radical anion/cation pair **5i** (see below), no doubt due to much extensive delocalization in the former species. Curiously enough, the vinylogous **12i** system also becomes planar[59] and shows some restricted rotation both around the corresponding C_{ipso}−C bond (1.453 Å) and the $C_{vinyl}-CH_2$-OMe, thereby suggesting that overlapping is crucial for understanding activation and cleavage in positions far away from the electron sink. In other words, by introducing an extra electron in an aromatic system such as **4** or the vinylogous species **11**, the system replies by activating the C−O bond (benzylic or vinylogous) for dissociation; i.e., the σ^* orbital is partially populated as demonstrated by its increased bond length and reduced bond order, regardless of whether the counterion is taken into consideration [**5i** (1.419 Å), [0.930]; **12i** (1.408 Å), [0.946]] or not [**5** (1.426 Å), [0.902]; **12** (1.416 Å), [0.918]]. These features (Figure 3) lend credit to the general assertion that stereoelectronic factors are extremely important in determining the rate of these type of cleavages[60] or, in terms of the mixed valence approach,[61] that a low energy barrier exists for reaching the σ^* state from the π^* state.

Cleavage: Haptomeric Activation. Subtle differences exist, however, in considering activation of the C−O bond toward dissociation for the different ion pair species, as evidenced by its bond length and bond order. Activation in SSIP's and IIP's is obviously related to the size of the conjugated π system and the stereoelectronic requirements for overlap, as shown by the fact that C−O activation in **5** is significantly more advanced [1.426 Å, [0.902] than in the vinylogous system **12** [(1.416 Å), [0.918]]. On the other hand, since reductive cleavage is in actuality a β elimination reaction, activation for dissociation in CIP species must be a function of the location of the counterion in regard with the leaving group heteroatom, itself a function of hapticity.[62] Herein, we use the term hapticity to indirectly define the site of the metal on the π system and propose the term haptomeric activation to define the extent to which the C−O bond is prepared for cleavage in the different haptomeric species along the reaction coordinate. As for benzyl-

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[59] This is remarkable in light of the well-known tendency of MNDO to overestimate repulsive steric repulsions.

[60] (a) Gerson, F.; Huber, W.; Mullen, K. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 208. (b) Gerson, F.; Moshuk, G.; Schwyzer, M. *Helv. Chim. Acta* **1971**, *54*, 361. (c) Bauld, N. L.; Hudson, C. E. *Tetrahedron Lett.* **1974**, 3174. (d) Dodd, J. R.; Pagni, R. M.; Watson, C. R. *J. Org. Chem.* **1981**, *46*, 1688. (e) Dodd, J. R.; Winton R. F.; Pagni, R. M.; Watson, C. R.; Bloor, J. *J. Am. Chem. Soc.* **1974**, *96*, 7846. (f) Rieke, R.; Ogliaruso, M.; McClung, R.; Winstein, S. *J. Am. Chem. Soc.* **1966**, *88*, 4729. (g) Nelson, S. F.; Gillespie, J. P. *J. Org. Chem.* **1973**, *38*, 3592. (h) Hartman, R. F.; Van Camp, J. R.; Rose, S. D. *J. Org. Chem.* **1987**, *52*, 2684. (i) Bauld, N. L.; Chang, C. S.; Farr, F. R. *J. Am. Chem. Soc.* **1972**, *94*, 7164.

[61] (a) Ratner, M. A. *Int. J. Quant. Chem.* **1978**, *14*, 675. (b) Hale, P. D.; Ratner, M. A. *Int. J. Quant. Chem.* **1984**, *18*, 195. (c) Wong, K. Y.; Schatz, P. N. *Prog. Inorg. Chem.* **1981**, *28*, 369.

[62] At least in one case calculations have been used to determine the position of the counterion. See: Bolton, J. R.; Goldberg, I. B. *J. Chem. Phys.* **1970**, *74*, 1965. For controversy with the electrostatic model, see: Brooles, J. J.; Rhine, W.; Stuky, G. *J. Am. Chem. Soc.* **1972**, *94*, 7346.

lithium itself,[15e] MNDO is capable of detecting a number of local minima in the potential hypersurface of the radical anion/cation species resulting from **4** or **11**, namely η^6 structures **5i** and **12i** and η^3 structures **6i** and **13i** (found to lay 9.3 and 4.2 kcal/mol higher in energy (ΔH) than precursors **5i** and **12i**, respectively). Of course, only one counterion-free species (**5** and **12** or **5(i)** and **12(i)**) was found. The increasing activation of the C−O bond in moving from **5i** (1.419 Å, [0.930]) to **6i** (1.440 Å, [0.880]) or from **12i** (1.408 Å, [0.946]) to **13i** (1.412 Å, [0.945]) can be assigned to the approaching of lithium to the OMe leaving group which induces an increase in strength of ionic and covalent forces. Eventually, the haptomer having a lithium atom β to the leaving group undergoes syn β elimination, as expected.[63] Transition state structures **TS6i** (1.963, [0.279]) and **TS13i** (1.995, [0.252]) clearly illustrate this assertion (Figure 3). On the other hand, β elimination in the case of counterion-free radical anions (either solvent separated (SSIP's) or the so-called isolated (IIP's)) should be of the E_{1cb} type. For these cases C−O bond cleavage is not assisted by the counterion, and in all cases, ΔG^* is larger than for the analogous CIP.

In accordance with the expected higher population of the σ^* orbital at the dianion stage, calculations clearly show that C−O activation for dissociation is significantly more advanced for the dianion species (Figure 4), as previously suggested by Walsh.[35] As for the above radical anion/cations, activation is induced during the reduction stage and as a consequence of haptomeric equilibria (for CIP's, only). Evidence for the former is found when the same indicators (enlarged C−O bond; reduced bond order) as above are examined for the CIP dilithio derivatives **9ii** **[**(1.420 Å), [0.923]] and **16ii** [(1.415 Å), [0.922]] resulting from BIHY and VIBIHY processes. Haptomeric activation for dissociation is evident when C−O bond parameters are examined for **10ii** **[**(1.423 Å), [0.915]], **17ii** [(1.415 Å), [0.917]], and **18ii** [(1.448 Å), [0.846]], the former in equilibrium with **9ii** and the last two with **16ii** (Figure 4). On the other hand, activation of the C−O bond for cleavage in IIP's **9** [(1.480 Å), [0.729]] and **16** [(1.460 Å), [0.771]] or SSIP's **9(ii)** [(1.428 Å, [0.882]] and **16(ii)** [(1.420 Å), [0.892]] is much more advanced as, in these cases, counterions do not serve the purpose of sharing electron density as in the case of CIP's.

The Radical Anion/Cation vs. Dianion/Dication Routes for Cleavage. According to our MNDO calculations, the question of whether reductive cleavage of benzyl ethers and the vinylogous cinnamyl systems involve radical anion/cation or dianion/dication species is also related to the nature of ion pairing as ΔG^* values (measured, in all cases, from the lowest energy precusors on the reaction coordinate) vary considerably with it. BIHY reactions, in particular, prefer to take place through transient radical anion/cation pairs (either CIP's or SSIP's or IIP's), the routes involving the corresponding dianion/dication pairs being more energy costly. Thus, for example, Birch reductive cleavage of **4** through transition structure **TS6i** was found to lie at $\Delta G^* = 36.8$ kcal/mol (43.0 kcal/mol in the case of **TS6(i)** and 45.6 kcal/mol for **TS6**, for the cleavage of SSIP and IIP, respectively), whereas transition structure **TS10ii** involving cleavage of the CIP dianion/dication species was found to lie at $\Delta G^* = 38.1$ kcal/mol (55.9 kcal/mol for **TS10(ii)** and 143.6 kcal/mol for **TS10**), as illustrated in Figure 5. When LiBenz was considered, instead of LiNaph, close values were obtained: $\Delta G^* = 38.1$ kcal/mol for **TS6i** and $\Delta G^* = 40.6$ kcal/mol for **TS10ii**. These results clearly suggest that *(1) the lowest energy route for BICLE reactions is that involving cleavage of radical anion/cation species, likely as CIP's, and (2) routes involving cleavage of CIP radical anion/cation species and dianion/dication species may actually compete in some particular cases (see below),* as experimentally demonstrated by Walsh.[35]

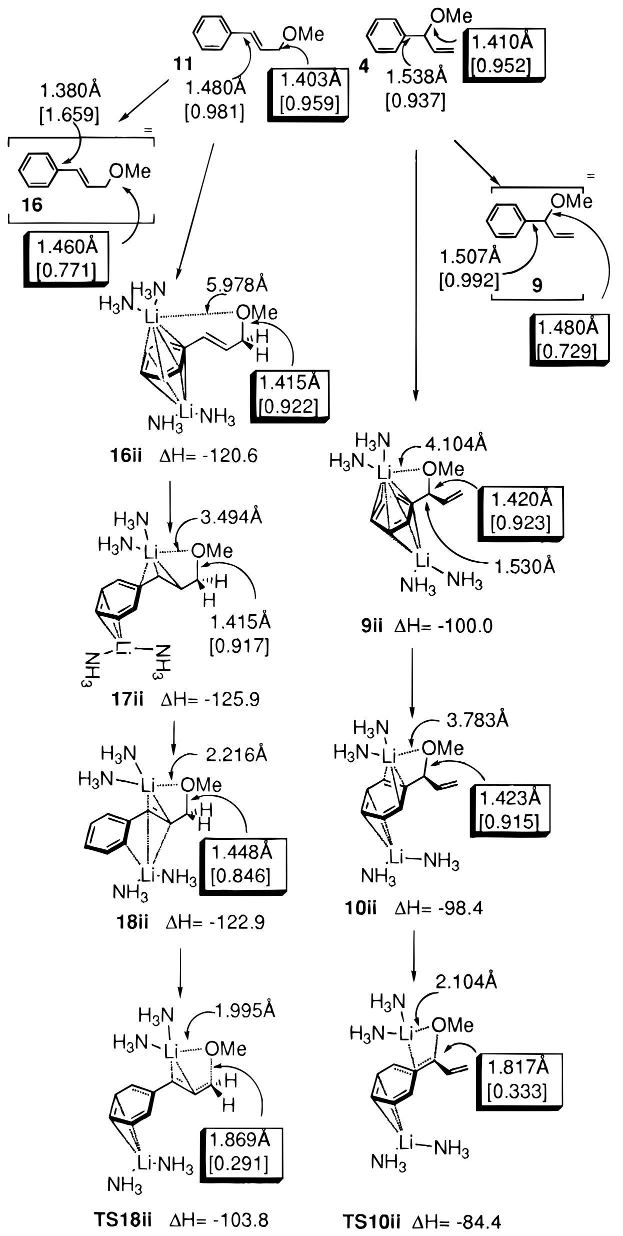

Figure 4. MNDO-determined structures of intermediates and transition states for the cleavage of benzyl and cinnamyl ethers **4** and **11** through dianion routes involving CIP's and IIP's (SSIP's species not shown). Geometrical features relevant to haptomeric activation are shown: (1) C−OMe bond length and bond order (in brackets); (2) Li−OMe distance; (3) enthalpy of formation.

In striking contrast with the above clear-cut analysis for BICLE processes, calculations show that VIBICLE reactions are a bit more complex as, now, the routes involving dianion/dication species (as CIP's or SSIP's, only) are kinetically favorable over those involving the

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(63) Wakefield, B. J. *The Chemistry of Organolithium Compounds*; Pergamon Press: New York, 1974.

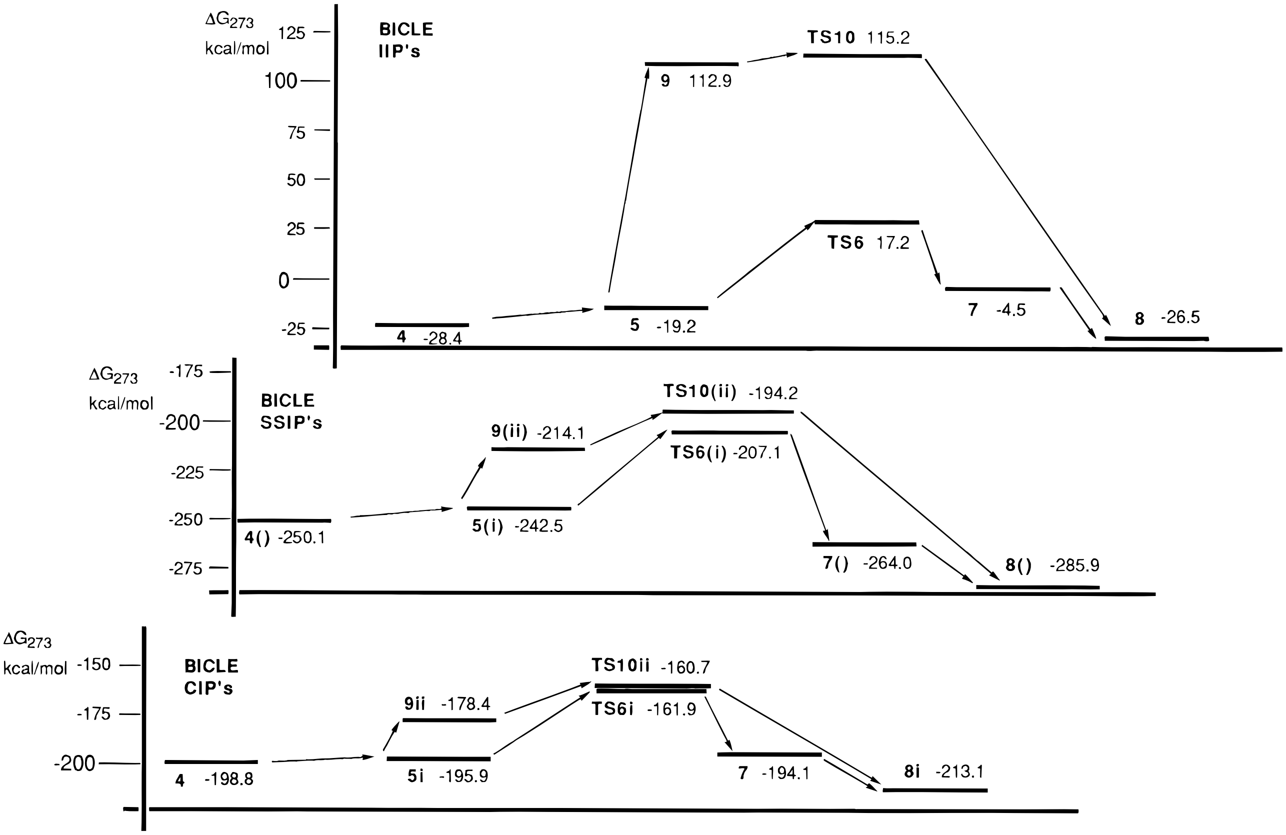

Figure 5. Energy (ΔG_{273}, kcal/mol) profiles for cleavage of benzyl ether **4** promoted by lithium naphthalenide through BICLE routes involving CIP's [**4** + $2Li(NH_3)_2Naph$ + $4NH_3$), SSIP's (**4** + $2(Li^+(NH_3)_4)$ + $2Naph^{-\bullet}$), and IIP's [**4** + $2(Li^+(NH_3)_4$ + $2Naph^{-\bullet}$]. Stoichiometry is mantained throughout in all calculations.

corresponding radical anion/cation species, except when the rather unrealistic IIP's are considered. The following data for VIBICLE processes concerning cinnamyl ether analog **11** illustrate this analysis: $\Delta G^* = 37.2$ kcal/mol for **TS13i** but only 28.9 kcal/mol for **TS18ii** for cleavage of CIPs, and $\Delta G^* = 42.0$ kcal/mol for **TS13(i)** but only 36.8 kcal/mol for **TS18(ii)**) for cleavage through SSIP (Figure 6). Calculations using LiBenz instead of LiNaph afforded closely related values for cleavage of CIP: ΔG^* = 37.5 kcal/mol for transition structure **13iTS** and 30.7 kcal/mol for **18iiTS**. Thus, *in accordance with MNDO calculations, reductive cleavage of cinnamyl derivatives (and, presumably of related systems as well) is clear-cut biased toward the dianion/dication routes when either CIP's or SSIP's are involved.*

Calculations on the 2-naphthyl analogs as CIP (supporting information) further insist on the generality of this phenomenon: whereas both BICLE processes (the so-called radical anion/cation and dianion/dication routes) for 2-(1′-methoxy-2-propen-1′-yl)naphthalene (**19**) promoted by LiNaph are energetically very close to one another ($\Delta G^* = 37.1$ and 36.6 kcal/mol, respectively), the corresponding VIBICLE routes for the conjugated analog (E)-2-(3′-methoxy-1′-propen-1′-yl)naphthalene (**20**) were found to be quite far apart in energy ($\Delta G^* = 35.9$ for the radical anion/cation route and 27.4 kcal/mol for the dianion/dication route).

So, according to these results, the question of whether reductive cleavage reactions involve radical anion/cation or dianion/dication pairs is difficult to predict *a priori*. Some trends, however, appear to be general. For extensively conjugated systems such as cinnamyl ether **11** and its naphthyl analog **20** the lowest energy route is that represented by steps **11** → **12i** → **16ii** → **17ii** → **18ii** → **15i** + MeOLi.[64] That for nonconjugated systems,[64] however, is even more difficult to predict on the basis of the above MNDO results, as both routes compete and either solvent, substrate, reductive agent, leaving group, carrier, or metal effects may, in a given case, divert the reaction toward one side or another.

An important consequence of kinetic significance which derives from the above analysis is that, *irrespective of whether radical anion/cation or dianion/dication species are involved in cleavage, the route of lowest energy barrier is that involving CIP's, those for SSIP's or IIP's being, in all cases, more energy costly.* This result might shed some light into some unsolved problems such as the experimental observation on radical anion species which are

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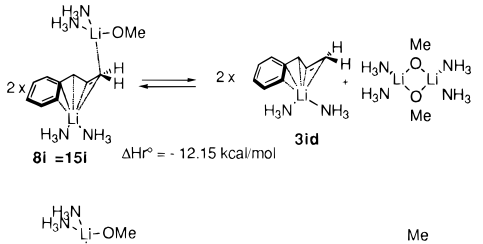
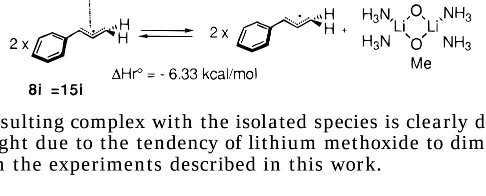
[64] MNDO calculations predict that complexation between either radical **7** or the final π organolithium compound **15i** (= **8i**) and lithium methoxide is possible. Nevertheless, the equilibrium (shown below)





of the resulting complex with the isolated species is clearly displaced to the right due to the tendency of lithium methoxide to dimerize, in line with the experiments described in this work.

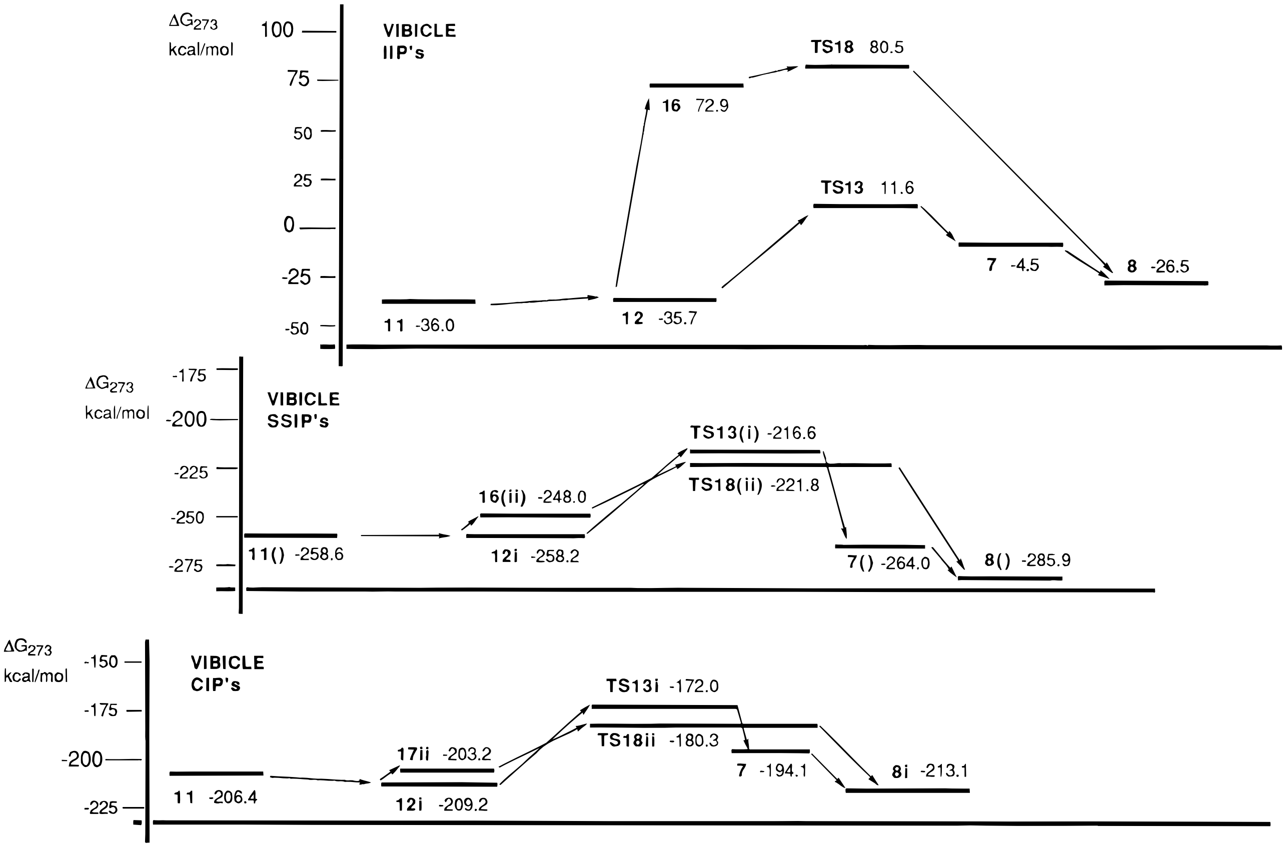


Figure 6. Energy (ΔG_{273}, kcal/mol) profiles for cleavage of cinnamyl ether **11** promoted by lithium naphthalenide through BICLE routes involving CIP's [**4** + $2Li(NH_3)_2Naph + 4NH_3$), SSIP's (**4** + $2(Li^+(NH_3)_4$)+ $2Naph^{-\bullet}$), and IIP's [**4** + $2(Li^+(NH_3)_4 + 2Naph^{-\bullet}$]. Stoichiometry is mantained throughout in all calculations.

longer lived when generated (by pulse radiolysis) in water than in DMF (electrochemically).[9f]

The answer to the central stereochemical issue which originated this study lies, according to MNDO, in the nature of the species suffering stepwise cleavage. The lowest energy route found for BICLE processes as applied to α-vinylbenzyl methyl ether (**4**) and related compounds involves cleavage of a radical anion/cation **5i** (a CIP species) which is less stable than starting materials and, therefore, does not accumulate. As only one chiral center (it is devoid of chiral plane) exists in **5i**, cleavage gives rise to a vinyl-substituted benzyl radical which retains the configuration of the vinyl grouping because further reduction to the final organolithium is much faster than equilibration. In striking contrast, the vinylogous Birch cleavage of cinnamyl derivative **11Me** (and, presumably, of related systems as well) leads to the intermediate formation of a long-lived radical anion/cation intermediate **12iMe** the most stable conformers of which (separated by just $\Delta G = 0.6$ kcal/mol) interconvert through low energy barrier processes (Figure 7). As shown above, the lowest energy route for VIBIHY cleavage involves not the radical anion/cation stage but the transient dianion/dication CIP species **18iiMe** resulting from subsequent reduction of **12iMe** by LiNaph. Since a chiral plane develops, eventually two diastereoisomeric transition states involving syn *β* elimination actually compete, namely **TS18iiMe** *E* and **TS18iiMe** *Z*. MNDO calculations show that $\Delta\Delta G^*$ for cleavage of the *E* ($\Delta G^* = +30.8$ kcal/mol) and *Z* ($\Delta G^* = +31.0$ kcal/mol) transition structures is 0.2 kcal/mol, which give rise to the corresponding *E* and *Z* organolithium species **3ic** in reasonably close agreement with the experimental facts.

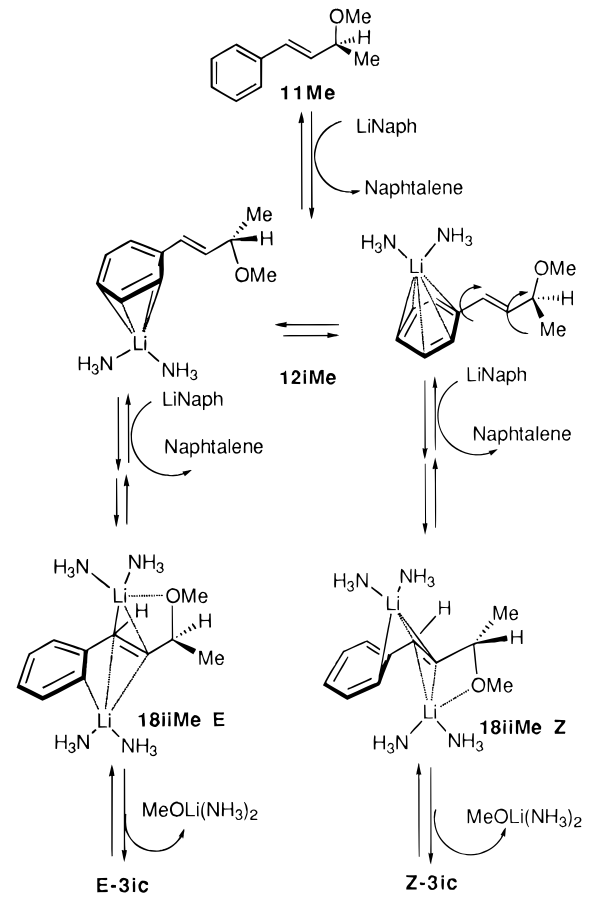


Figure 7. Stereochemical bias for cleavage of **11Me**.

In summary, metal-mediated Birch and vinylogous Birch cleavage reactions has been experimentally demonstrated to give rise to η^3 vinyl-substituted benzyllithiums which do not undergo isomerization at the temperature (<0 °C) of operation. ^{6}Li$-^1$H HOESY experiments proved that these species do not form mixed aggregates with the lithium silyloxide cogenerated in the reaction. Extensive semiempirical (MNDO) calculations have shed some light to the stereochemical problem as well as to the more general subject of the role of counterions and solvent in metal-promoted (lithium) reductive cleavage reactions. A simplified model for contact, solvent-separated, and isolated ion pairs has allowed us to evaluate these complex reactions in some detail. In particular, our studies on model compounds of the Birch and vinylogous Birch cleavage reactions (BICLE and VIBICLE) suggest the following: (a) the lowest energy routes for cleavage are, in all cases, those involving contact ion pairs in which the (lithium) counterion plays a key role by assisting the leaving group to depart through a syn β elimination pathway; (b) haptomers of the CIP's radical anion/cation or the dianion/dication species are key for appropriately understanding the cleavage step; (c) routes involving counterion-free species, either as solvent-separated or isolated, nonsolvated ion pairs are more energy costly, in all cases; (d) according to MNDO, the lithium-promoted cleavage of benzyl derivatives (BICLE) is a stepwise process involving transient radical anion/cation species, whereas the lowest route for cleavage of cinnamyl derivatives (VIBICLE), also stepwise, is that of the dianion/dication species; and (e) the puzzling stereochemistry observed for BICLE and VIBICLE reactions is a consequence of the fact that there are two competing diastereomeric transition states for the latter due to the existence of a chiral plane, but only one for the former which does not have chiral plane. According to this reasoning, one is tempted to predict that dissociative electron transfer, disregarding the actual stage at which cleavage occurs, can also take place at more distant sites of the electron sink provided that haptomeric equilibria allows it. To the best of our knowledge this is the first time calculations predict the existence of haptomers in anion radicals.[29] In our view, the above results should be of value for understanding cleavage reactions promoted by electrochemical means or otherwise.

Experimental Section

General Methods. Measuring frequencies were 300.1 MHz (^{1}H), 75.4 MHz (^{13}C), and 44.1 MHz (^{6}Li). Quadrature detection was carried out in both dimensions for 2D spectra. Proton, carbon-13, and lithium-6 NMR spectra were obtained in THF-d_8, the former two being referenced to the residual tetrahydrofuran peaks at 3.58 ppm and 67.4 ppm, respectively. Lithium-6 spectra were referenced to 1 M LiCl in D_2O. 2D ^{6}Li$-^1$H HOESY spectra[50] were recorded at -20 °C (mixing time = 1.8 s, D1 = 3 s, 256 increments in t_1, 32 scans acquired in ^{6}Li per increment, 1 K data points collected per scan, total measuring time = 12 h). Lithium-6 was purchased from Aldrich. Commercial THF-d_8 was distilled from sodium benzophenone ketyl under argon. Compounds **1a**, (*E*)-**1b** (containing 5% of Z isomer), (*Z*)-**1b** (containing 8% of E isomer) and (*E*)-**2b** were prepared following the described methodology[5c] and their stereochemical purity (where appropriate) determined by NMR.

Preparation of NMR Samples. Freshly cut pieces of lithium wire (3 mol) were placed inside a previously dried (oven; cooled under argon) 5-mm NMR tube which was then inmediately fitted with a serum cap. A solution of 0.5 mmol of precursors **1** or **2** in 0.5 mL of dried THF-d_8 was added via syringe. The tubes were then flamed-sealed under argon. The mixture was briefly sonicated a 0 °C until reaction starts and left aside at -25 °C for 48 h. The thus obtained deep orange-red solutions of **3i** were stable for at least 2 months at -20 °C.

3ia: ^{1}H NMR (243 K) δ: 6.35 (1H, t, $J = 7.7$ Hz), 6.23 (1H, d, $J = 7.8$ Hz), 6.14 (1H, d, $J = 7.8$ Hz), 6.06 (1H, d, $J = 11.8$ Hz), 5.86 (1H, d, $J = 7.7$ Hz), 5.25 (1H, t, $J = 6.7$ Hz), 3.40 (1H, d, $J = 11.8$ Hz), 1.8 (3H, s), 0.01 (9H, s, $LiOSiMe_3$) ppm; ^{13}C NMR (243 K) δ 149.8, 130.3, 129.7, 128.5, 119.1, 111.6, 104.4, 93.5, 29.0, 20.2, 6.5 ($LiOSiMe_3$) ppm; ^{6}Li NMR δ 3.03, 2.18 ppm.

(*Z*)-3ib: ^{1}H NMR (253 K) δ 6.38 (1H, t, $J = 7.1$ Hz), 6.29 (1H, t, $J = 7.3$ Hz), 6.19 (1H, d, $J = 9.6$ Hz), 6.08 (1H, d, $J = 11.9$ Hz), 5.88 (1H, d, $J = 8$ Hz), 5.23$-$5.18 (2H, br m), 3.76 (d,1H, $J = 11.7$ Hz), 2.02 (4H,m), 1.79 (3H, s), 1.77 (3H, s), 1.67 (3H, s), 0.00 (9H, s; $LiOSiMe_3$) ppm; ^{13}C NMR (253 K) δ 149.0, 131.1, 130.4, 129.6, 129.0, 128.6, 119.0, 111.2, 103.8, 97.7, 73.5, 36.0, 28.7, 27.7, 27.0, 19.4, 6.5 ($LiOSiMe_3$) ppm; ^{6}Li NMR δ 3.03, 2.18 ppm.

(*E*)-3ib: ^{1}H NMR (253 K) δ 6.35 (1H, t, $J = 7.2$ Hz), 6.23 (1H, t, $J = 7.2$ Hz), 6.15$-$6.10 (2H, m), 5.86 (1H, d, $J =$ 8Hz), 5.32$-$5.12 (2H, br m), 3.63 (d, 1H, $J = 11.9$ Hz), 2.13$-$2.08 (4H, m), 1.67 (3H, s), 1.64 (3H, s), 1.63 (3H, s), 0.01 (9H, s, $LiOSiMe_3$) ppm; ^{13}C NMR (253 K) δ 149.2, 131.1, 130.3, 129.9, 129.0, 128.5, 119.2, 111.5, 104.3, 97.8, 73.5, 44.7, 31.7, 27.7, 19.4, 18.5, 6.5 ($LiOSiMe_3$) ppm; ^{6}Li NMR δ 3.03, 2.18 ppm.

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Supporting Information Available: Tables containing *Z* matrices and GNORMs of the optimized molecular structures and the ^{6}Li$-^1$H HOESY spectra of **3ia**, (*E*)-**3ib**, and (*Z*)-**3ib** are provided (46 pages). This material is contained in libraries on microfiche, inmediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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