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Dearomatizing Anionic Cyclization and Novel Skeletal Rearrangement: High Yield Formation of Multiply Substituted Bicyclic or Polycyclic Spirocyclopentadienes and Phenanthrene Derivatives from 4-Aryl 1-Lithio-1,3-butadienes

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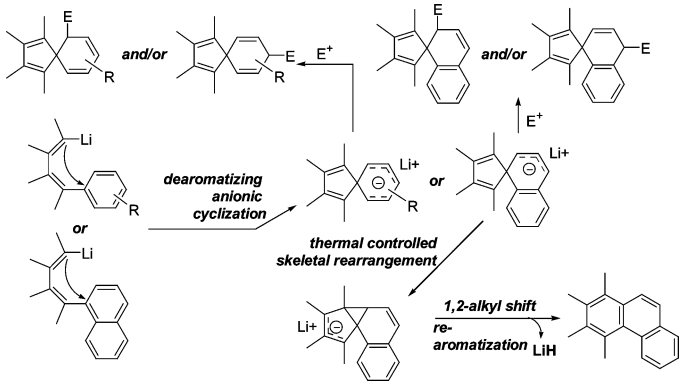

Both 4-phenyl 1-lithio-1,3-butadienes and 4-naphthyl 1-lithio-1,3-butadienes underwent highly efficient and selective intramolecular nucleophilic addition of the butadienyllithium to the aromatic rings, resulting in full dearomatization of the phenyl rings and partial dearomatization of the naphthyl rings. When the reactions were carried out at lower temperatures, ipso intramolecular nucleophilic attack took place exclusively to afford the spirocyclopentadiene derivatives upon hydrolysis or further treatment with a variety of electrophiles. 4-Naphthyl 1-lithio-1,3-butadienes and 4-phenyl 1-lithio-1,3-butadienes were found to proceed in this reaction under similar conditions, with the former being faster even at −78 °C. However, when the reaction of 4-naphthyl 1-lithio-1,3-butadienes was carried out at higher temperatures, such as 75 °C, an interesting skeletal rearrangement took place to afford the vicinal attack products, tetrasubstituted phenanthrenes, via a dearomatization/rearomatization process. Mechanistic investigation revealed that the kinetically favored ipso attack intermediates might undergo thermal skeletal rearrangement via 1,2-alkyl shift.

Introduction

Activation and application of unreactive molecular structures including the stable π-system of aromatic rings is a great challenge in organic synthesis. The coordination of transition metals with aromatic rings[1−7] and the addition of main group organometallic reagents to aromatic compounds[8−17] are among the most frequently used methods for dearomatizing the stable

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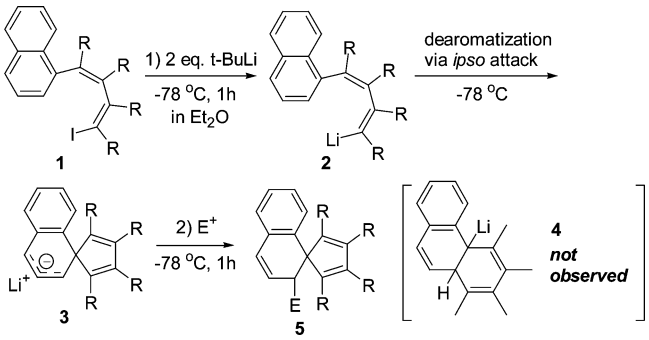
π-system of aromatic rings. In particular, the intramolecular nucleophilic addition of organolithium to aromatic rings has become one of the most efficient approaches to break the π-system of arenes.[12−17] A variety of functionalized bicyclic, polycyclic, and spiro compounds can be thus prepared using this approach. In principle, electron-deficient aromatic rings bearing electron-withdrawing groups, such as carbonyl groups, amides including *N*-benzyl benzamides, *N*-benzyl naphthamides, sulfonamides, and phosphonamides, etc., are extensively studied by the Clayden[12−16] and Lopez-Ortiz groups[17] because these types of aromatic compounds can efficiently undergo nucleophilic attack leading to various useful compounds.[11−17]

Recently, we have communicated dearomatizing anionic cyclization of 4-naphthyl 1-lithio-1,3-butadienes **2**, which was generated in situ quantitatively from their corresponding iodo compounds **1** (Scheme 1).[18] Several features of this reaction can be depicted as follows. (1) This reaction at −78 °C resulted in the formation of the spirocyclopentadiene intermediates **3**, obviously via ipso intramolecular nucleophilic attack, which is rarely observed in dearomatization reactions.[2,5,15] The commonly obtained fused ring products **4** and related compounds via vicinal attack were not formed at all under the reaction conditions. Furthermore, the dearomatized organolithium intermediates **3** can react with a variety of electrophiles to afford spiro tricyclic compounds **5** with different substituents. (2) The butadienyllithium (sp^2C-Li) as a nucleophile to attack the aromatic rings is unprecedented. It is of special interest because the useful butadienyl skeleton can be integrated with the aromatic rings. (3) The aromatic ring (here naphthalene) is unactivated. Fewer examples are known for dearomatization of unactivated aromatic rings.[15,19]

SCHEME 1. Dearomatizing Anionic Cyclization of 1-Lithio-4-naphthyl-1,3-butadienes Followed by Reaction with Electrophiles: Formation of Spirocyclopentadiene Derivatives



During our further investigation into this unique reaction, we found that, in addition to the naphthyl ring in 4-naphthyl 1-lithio-1,3-butadienes **2**, the phenyl ring in 4-phenyl 1-lithio-1,3-butadienes could also undergo the dearomatizing anionic cyclization. More interestingly, we found that the kinetically favored ipso attack intermediates underwent a novel thermal skeletal rearrangement to afford the vicinal products, tetrasubstituted phenanthrenes, via a dearomatization/1,2-alkyl shift/rearomatization process. In this paper, we report the scope and limitations of this synthetically useful reaction.

Results and Discussion

Intramolecular Dearomatizing ipso Attack of Butadienyllithium to Naphthyl Rings in 4-Naphthyl 1-Lithio-1,3-butadienes and to Phenyl Rings in 4-Phenyl 1-Lithio-1,3-butadienes, Affording Spirocyclopentadiene Derivatives and Further C−C Bond Forming Applications. 4-Aryl 1-lithio-1,3-butadiene derivatives used in this research, including 4-naphthyl, 4-phenyl, and 4-(substituted phenyl) 1-lithio-1,3-butadiene derivatives, were quantitatively generated in situ from their corresponding 4-aryl 1-iodo-1,3-butadienes by lithium−halogen exchange with *t*-BuLi. 4-Aryl 1-iodo-1,3-butadiene derivatives could be readily prepared in high isolation yields in one pot from alkynes and aryl halides mediated by the cooperation of low-valent zirconocene species with copper salts.[20] Thus, when 1-iodo-4-naphthyl-1,3-butadiene **1a** (R = Et) was treated with 2 equiv of *t*-BuLi at −78 °C, no formation of the corresponding monolithio reagent **2** was observed upon hydrolysis with aqueous $NaHCO_3$ at −78 °C. Instead, we

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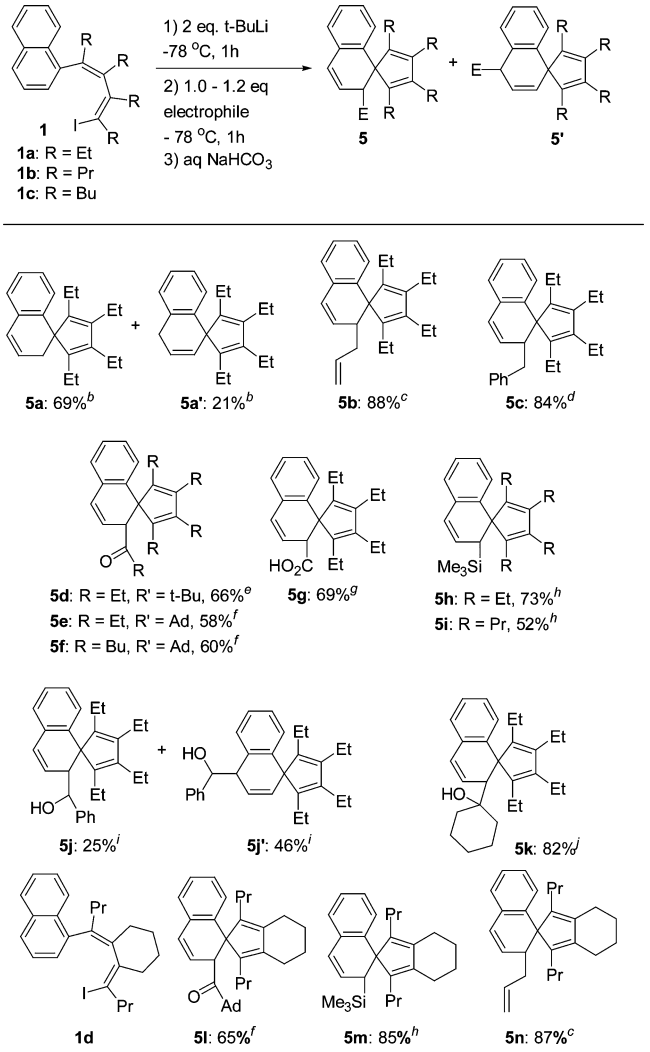
TABLE 1. Spirocyclopentadiene Products from Dearomatizing Anionic Cyclization of 1-Lithio-4-naphthyl-1,3-butadienes Followed by Reactions with Electrophiles[a]



[a] Isolated yields. [b] Hydrolyzed mixture of products using aqueous $NaHCO_3$. [c] From allyl bromide. [d] From benzyl bromide. [e] From *t*-BuCOCl. [f] From AdCOCl. [g] From CO_2, hydrolyzed using aqueous NH_4Cl. Structure was determined by X-ray crystal analysis. [h] From $SiMe_3Cl$. [i] Reaction with PhCHO followed by quench using aqueous $NaHCO_3$. [j] From cyclohexanone.

isolated the spiro tricyclic products **5a** and **5a′** as double bond positional isomers (**5a**: 69% yield, **5a′**: 21% yield) in 90% combined yield (Table 1). This result indicated that the in situ generated 4-naphthyl 1-lithio-1,3-butadiene **2a** was very reactive even at −78 °C to undergo the unusual dearomatizing anionic cyclization, forming the type of anionic species **3** as shown in Scheme 1.

As demonstrated in Table 1, 4-naphthyl 1-iodo-1,3-butadiene derivatives **1a**−**d** could all undergo this rapid sequential lithium−iodo exchange/dearomatizing anionic cyclization process to give the anionic species **3**. These corresponding lithiated intermediates **3** could be applied further to form new C−C bonds with a variety of electrophiles. Very interestingly, depending on the nature of electrophiles, either a mixture of regioisomers or a sole product of high regioselectivity was obtained, all in excellent isolated yields. For example, electrophiles such allyl bromide (**5b**), benzyl bromide (**5c**), acid chlorides (**5d**, **5e**, **5f**), CO_2 (**5g**), and Me_3SiCl (**5h**, **5i**) gave only one product. Ketones and aldehydes could also be applied, but aldehydes afforded a

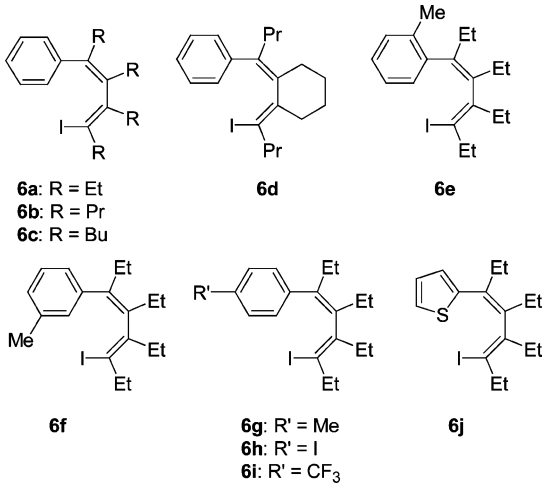


FIGURE 1. A variety of 4-phenyl 1-iodo-1,3-butadienes used in this research.

mixture of separable double bond positional isomers (**5j** and **5j′**), while ketones gave only one product (**5k**). When **1d** was used, the tetracyclic spiro compounds (**5l**, **5m**, **5n**) could be obtained in high yields.

It should be mentioned that at this temperature only the ipso attack products, the spiro compounds **5** and/or **5′**, were obtained. The usually observed vicinal intramolecular nucleophilic attack products were not observed at all.

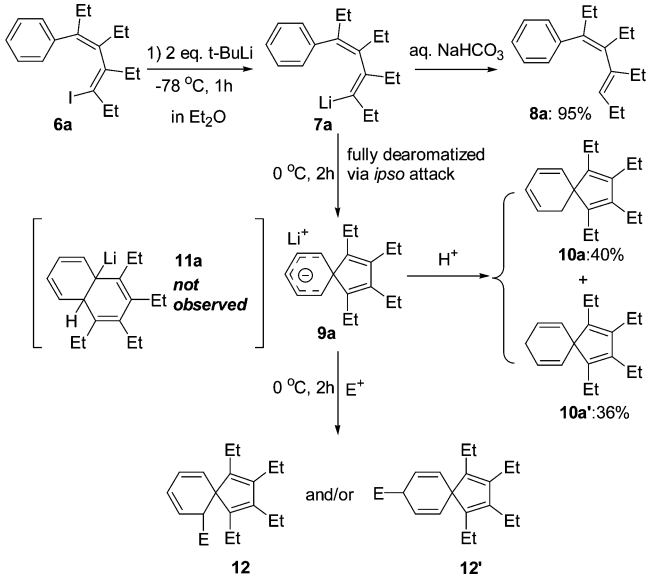
Prompted by the unusual reaction of 4-naphthyl 1-lithio-1,3-butadienes, we investigated the reaction of analogous 4-phenyl 1-lithio-1,3-butadiene derivatives. Listed in Figure 1 are 4-phenyl 1-iodo-1,3-butadienes used in this research.[20] These compounds were prepared following the literature procedure and could be obtained in high isolated yields.[20] They can be readily transformed to their corresponding 4-phenyl 1-lithio-1,3-butadiene derivatives via lithium−iodo exchange when they were subject to reactions.

Initially, as shown in Scheme 2, we carried out the reaction of **6a** with 2 equiv of *t*-BuLi at −78 °C. We did observe the lithium−iodo exchange affording the hydrolyzed product **8a** in 95% isolated yield upon quench with aqueous $NaHCO_3$. However, on the contrary, this monolithium reagent **7** was stable at −78 °C. Totally no dearomatizing anionic cyclization took place. It was also stable even at −50 °C. This is in sharp contrast to the reactivity of **2** as described above. We then increased the reaction temperature to 0 °C, and we found dearomatizing anionic cyclization took place and completed after 2 h at this temperature. Hydrolysis of the reaction mixture with aqueous $NaHCO_3$ afforded a mixture of two double bond positional isomers **10a** and **10a′** in 40 and 36% isolated yields, respectively.

It should be mentioned that at this temperature the usually observed vicinal intramolecular nucleophilic attack products of the type **11a** or related compounds were not observed at all.

To further demonstrate the usefulness of this reaction, we treated the lithiated intermediates **9** with a variety of electrophiles. Shown in Table 2 are examples obtained from the reaction of **9a** with aldehydes, ketones, and imine PhCH═NPh. Representative structures are given as **12** and **12′**. All products were obtained in good isolation yields. Although mixtures of double bond positional isomers were obtained (entries 1−8),

SCHEME 2. Dearomatizing Anionic Cyclization of 1-Lithio-4-phenyl-1,3-butadienes Followed by Reaction with Electrophiles: Formation of Spirocyclopentadiene Derivatives



they could be easily separated using column chromatography. In the case of bulky *t*-BuCHO (entry 9), only the isomer **12j′** was formed. For the reaction of **9a** with ketones and PhCH═NPh (entries 10−12), isomers **12′** were generally obtained, probably due to steric effect.

We then applied other 4-phenyl 1-lithio-1,3-butadiene derivatives which could be readily generated in situ from their corresponding 4-phenyl 1-iodo-1,3-butadienes (**6b**−**j**) given in Figure 1. Results are shown in Figure 2. As expected, 4-phenyl 1-lithio-1,3-butadiene derivatives (**6b**−**d**) reacted with aldehydes, ketones, and/or PhCH═NPh in a similar manner compared with **6a**, but the substituted phenyl rings behaved differently from each other. For example, the *o*-methyl phenyl ring **6e** underwent the intramolecular nucleophilic attack similarly with the nonsubstituted phenyl rings **6a**−**d**, affording **19** in 57% isolated yield from its reaction with cyclopentanenone. The *m*-methyl phenyl ring (**6f**) could also undergo the reaction. However, the *p*-substituted phenyl rings (**6g**: Me, **6h**: I, **6i**: CF_3) did not show any cyclization reactions, even in

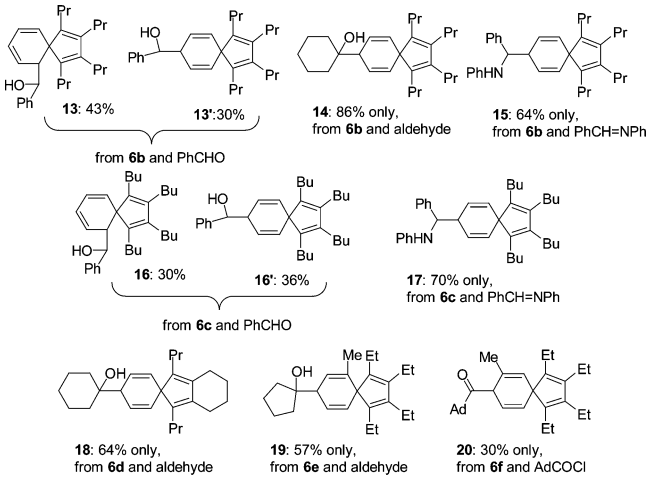
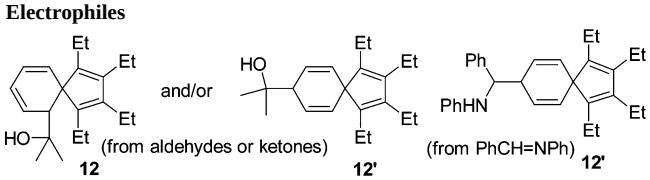
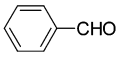
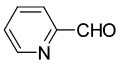
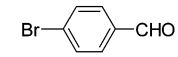
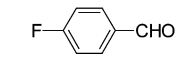
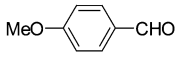
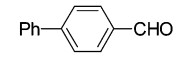
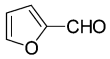
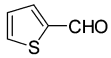


FIGURE 2. More examples of spirocyclopentadienes using **6b**−**f** (isolated yields).

TABLE 2. Treatment of the Reaction Mixture 9a with Electrophiles

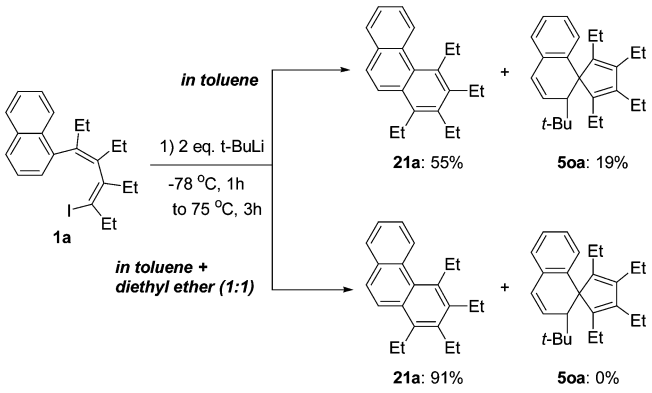


entry	electrophile	yield of **12** (%)	yield of **12'** (%)	total isolated yield (%)
1		**12a**: 26	**12a'**: 52	78
2		**12b**: 23	**12b'**: 43	66
3		**12c**: 53	**12c'**: 35	88
4		**12d**: 28	**12d'**: 44	72
5		**12e**: 31	**12e'**: 50	81
6		**12f**: 48	**12f'**: 21	69
7		**12g**: 37	**12g'**: 33	70
8		**12h**: 31	**12h'**: 29	60
9	t-Bu−CHO	**12i**: 0	**12i'**: 52	52
10		**12j**: 0	**12j'**: 75	75
11		**12k**: 0	**12k'**: 50	50
12	PhCH=NPh	**12l**: 0	**12l'**: 77	77

the case of the very strong electron-withdrawing group CF_3. These results demonstrate that the electronic effect, which makes the phenyl ring more electron-deficient, may not be the major reason for the dearomatizing anionic cyclization. The steric effect and the stability of the thus generated dearomatized species are assumed to be the major factors. In addition, the thienyl iodobutadiene **6j** could undergo the lithium−iodo exchange, but no dearomatizing cyclization took place even in refluxing toluene.

Formation of Tetrasubstituted Phenanthrene Derivatives via Novel Skeletal Rearrangement of the ipso Attack Intermediates Followed by Rearomatization. As described above, the dearomatization cyclization took place very fast even at −78 °C for 4-naphthyl 1-lithio-1,3-butadienes. In the case of 4-phenyl 1-lithio-1,3-butadienes, the dearomatization cyclization proceeded relatively slowly and a higher temperature (0 °C) was required. In order to investigate whether or not these types of compounds can undergo the commonly observed vicinal attack to afford the fused ring compounds, such as tetrasubstituted phenanthrene derivatives,[21−25] we screened reaction conditions. Initially, we used toluene as the solvent and carried out the reaction of **1a** with 2 equiv of *t*-BuLi from lower temperatures to 75 °C. Surprisingly, when the reaction mixture was stirred at 75 °C for 3 h, the desired product, tetraethyl-substituted

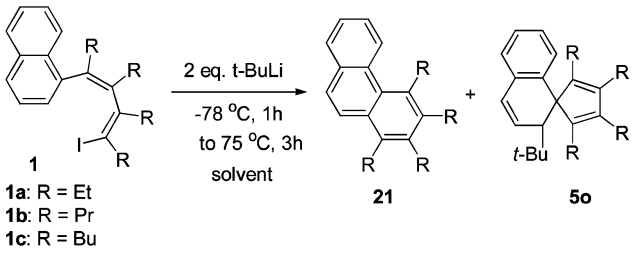
SCHEME 3. Formation of Tetraethyl Phenanthrene Derivative 21a: Solvent Effect

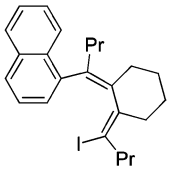
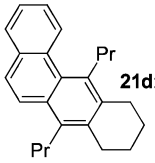


phenanthrene derivative **21a**, was indeed formed in 55% isolated yield (Scheme 3). In addition to the expected **21a**, an unexpected product, the *tert*-butylated **5oa** was also obtained in 19% isolated yield. Due to the formation of **5oa**, the expected **21a** was formed in unsatisfactory yields. The formation of **5oa** can be explained by that the in situ generated *t*-BuI from **1a** and *t*-BuLi does not react smoothly enough with another molecule of *t*-BuLi in toluene to get consumed. Thus, the later generated dearomatized lithiated intermediates **3** are trapped partially by the remaining *t*-BuI to afford the *tert*-butylated **5oa**.

To increase the yield of **21a**, the formation of **5oa** should be avoided. From the above analysis, we tried to use more polar solvents including mixed solvents to promote the complete and fast consumption of the in situ generated *t*-BuI. Finally, as shown in Scheme 3, we found when a 1:1 mixed solvent of diethyl ether and toluene was used and the reaction mixture of 4-naphthyl 1-iodo-1,3-butadiene **1a** and *t*-BuLi was heated up to 75 °C the phenanthrene derivative **21a** was formed very cleanly and obtained in 91% isolated yield. Formation of the *tert*-butylated **5oa** was completely suppressed. Listed in Table 3 are representative results of phenanthrene derivatives obtained in the above-described two different conditions, and the formation of **5o** is also given for comparison. Substituted phenanthrene derivatives can be thus prepared in excellent isolated yields. These types of fused ring compounds are very important and have attracted much recent attention as new organic materials.[21−25] This reaction provides an efficient method for these types of compounds.

TABLE 3. Preparation of Substituted Phenanthrene Derivatives 21



iodobutadiene **1**	solvent[a]	yield of product %[b] **21**	**5o**
1a	A	**21a**: 91	**5oa**: 0
	B	**21a**: 55	**5oa**: 19
1b	A	**21b**: 92	**5ob**: 0
	B	**21b**: 72	**50b**: 17
1c	A	**21c**: 83	**5oc**: 0
	B	**21c**: 56	**5oc**: 19
 **1d**	A	 **21d**: 90	0

[a] A: Toluene/Et_2O = 1:1; B: Toluene. [b] Isolated yield.

What interested us much more was how the vicinal attack products, the tetrasubstituted phenanthrenes **21**, were generated from the reaction mixture. As we mentioned above, the ipso attack of 4-naphthyl 1-lithio-1,3-butadienes took place very easily even at −78 °C. The formation of the phenanthrene derivatives **21** was really a surprise to us, though it was what we expected. Obviously, the formation of phenanthrene derivatives **21** was under thermodynamic control. Thus we carried out a series of experiments to obtain evidence.

To obtain direct experimental evidence, we carried out the reactions and analyzed the products at different reaction temperatures. First, we used toluene as the solvent; this was aimed at, in addition to understanding the mechanism for the formation of phenanthrene derivatives **21**, ensuring the formation of the *tert*-butylated **5o**. As can be seen from Table 4, when the reaction was carried out in toluene at −78 °C for 2 h (entry 1), half of the starting monoiodo compound **1a** remained unlithiated, indicating that the solvent is crucial for the lithiation reaction. On the other hand, this result also demonstrated that

(21) For reviews on preparation of substituted naphthalenes, see: (a) de Koning, C. B.; Rousseau, A. L.; van Otterlo, W. A. L. *Tetrahedron* **2003**, *59*, 7−36. (b) Yamamoto, Y. *Curr. Org. Chem.* **2005**, *9*, 503−519. (c) Lautens, M.; Alberico, D.; Bressy, C.; Fang, Y.; Mariampillai, B.; Wilhelm, T. *Pure Appl. Chem.* **2006**, *78*, 351−361. (d) Larock, R. C. *J. Organomet. Chem.* **1999**, *576*, 111−124.

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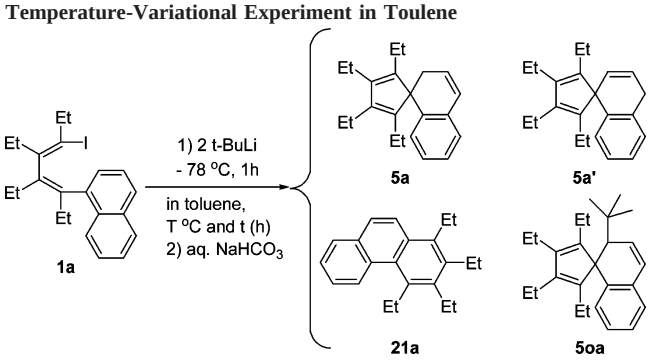
(23) (a) Takahashi, T.; Hara, R.; Nishihara, Y.; Kotora, M. *J. Am. Chem. Soc.* **1996**, *118*, 5154−5155. (b) Takahashi, T.; Kitamura, M.; Shen, B.; Nakaima, K. *J. Am. Chem. Soc.* **2000**, *122*, 12876−12878. (c) Duan, Z.; Nakajima, K.; Takahashi, T. *Chem. Commun.* **2001**, 1672−1673. (d) Huang, W.; Zhou, X.; Kanno, K.; Takahashi, T. *Org. Lett.* **2004**, *6*, 2429−2431. (e) Zhou, X.; Wang, H.; Kitamura, M.; Kanno, K.; Nakajima, K.; Takahashi, T. *J. Org. Chem.* **2004**, *69*, 4559−4562. (f) Kanno, K.-i.; Liu, Y.; Iesato, A.; Nakajima, K.; Takahashi, T. *Org. Lett.* **2005**, *7*, 5453−5456. (g) Takahashi, T.; Li, S.; Huang, W.; Kong, F.; Nakajima, K.; Shen, B.; Ohe, T.; Kanno, K. *J. Org. Chem.* **2006**, *71*, 7967−7977. (h) Yasukawa, T.; Satoh, T.; Miura, M.; Nomura, M. *J. Am. Chem. Soc.* **2002**, *124*, 12680−12681.

(24) (a) Johnson, S. A.; Liu, F.; Suh, M. C.; Zurcher, S.; Haufe, M.; Mao, S. S. H.; Tilley, T. D. *J. Am. Chem. Soc.* **2003**, *125*, 4199−4211. (b) Ramakrishna, T. V. V.; Sharp, P. R. *Org. Lett.* **2003**, *5*, 877−879. (c) Barluenga, J.; Vazquez-Villa, H.; Ballesteros, A.; Gonzalez, J. M. *Org. Lett.* **2003**, *5*, 4121−4123. (d) Yasukawa, T.; Satoh, T.; Miura, M.; Nomura, M. *J. Am. Chem. Soc.* **2002**, *124*, 12680−12681. (e) Larock, R. C.; Tian, Q. *J. Org. Chem.* **1998**, *63*, 2002−2009. (f) Larock, R. C.; Doty, M. J.; Tian, Q.; Zenner, J. M. *J. Org. Chem.* **1997**, *62*, 7536−7537.

(25) For substituted anthracenes, see: (a) Wang, Y.; Xu, J.; Burton, D. J. *J. Org. Chem.* **2006**, *71*, 7780−7784. (b) Harrowven, D. C.; Guy, I. L.; Nanson, L. *Angew. Chem., Int. Ed.* **2006**, *45*, 2242−2245. (c) Takahashi, T.; Li, Y.; Stepnicka, P.; Kitamura, M.; Liu, Y.; Nakajima, K.; Kotora, M. *J. Am. Chem. Soc.* **2002**, *124*, 576−582. (d) Qiao, X.; Ho, D. M.; Pascal, R. A., Jr. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1531−1532.

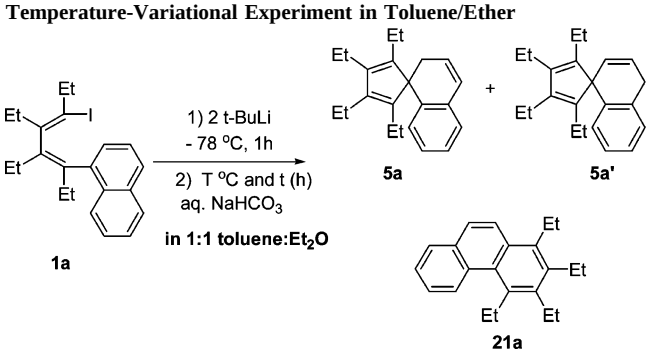
TABLE 4. Investigation into the Reaction Mechanisms: Temperature-Variational Experiment in Toulene



entry	*T* (°C)	time (h)	Yield of Product %[a] 1a	5a+5a′	21a	5oa
1	−78	2	54	29	2	9
2	0	1	0	46	11	33
3	rt	3	0	29	22	33
4	50	1	0	21	32	35
5	50	3	0	6	54	31
6	75	1	0	6	59	28
7	75	3	0	6	57(55)	29(19)

[a] GC yields. Isolated yields are given in parentheses.

TABLE 5. Investigation into the Reaction Mechanisms: Temperature-Variational Experiment in Toluene/Ether



entry	*T* (°C)	time (h)	Yield of Product %[a] (5a+5a′)[b]	21a
1	−78	1	89	0
2	0	2	91	0
3	rt	3	86	<3
4	50	1	39	44
5	50	2	18	67
6	75	1	trace	90
7	75	3	trace	91

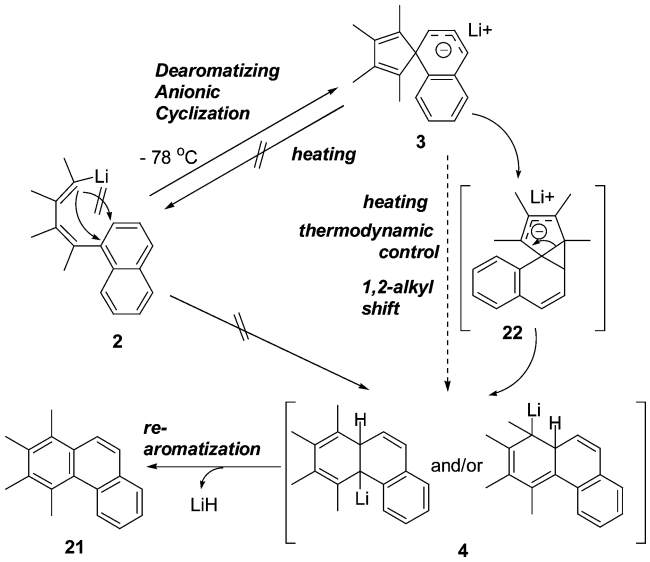
[a] Isolated yields. [b] A mixture of **5a** and **5a′** in 1:0.3 molar ratio. Combined isolated yields.

even in toluene, once 4-naphthyl 1-lithio-1,3-butadienes **2** were formed, dearomatization cyclization took place immediately at −78 °C. In addition to the dearomatization products **5a** and **5a′** in 29% yield, the *tert*-butylated **5oa** was also already formed in 9% yield. After the reaction temperature was increased to 0 °C for 1 h (entry 2), the starting monoiodo compound **1a** disappeared, affording 46% of the dearomatization products **5a** and **5a′** and 33% of **5oa**. At this temperature, the phenanthrene derivative **21a** appeared and was obtained in 11% yield. When the reaction temperature was further increased to room temperature, 50 °C, and higher (entries 3−7), the dearomatization products **5a** and **5a′** disappeared gradually, while the phenanthrene derivative **21a** became the major product. Under these conditions, the yield of the *tert*-butylated **5oa** became steady around 30%. This result indicated that *t*-BuI was quickly consumed at over 0 °C even in toluene.

The temperature-dependent experiments in the mixed solvent (toluene/diethyl ether = 1:1) gave more instructive information for the formation of the phenanthrene derivative **21a** from the dearomatization products (**5a** and **5a′**). As shown in Table 5, the dearomatization products (**5a** and **5a′**) were formed cleanly at −78 °C within 1 h and obtained in excellent isolated yields. This result also demonstrated that the lithium−iodo exchange reaction in this mixed solvent proceeded smoothly. At over room temperature, the phenanthrene derivative **21a** appeared, while the dearomatization products decreased. At 50 °C for 1 h, more than half of the dearomatization products were transformed to the phenanthrene derivative **21a** (entry 4). When the reaction temperature was increased to 75 °C for 1 h, the dearomatization products disappeared completely, resulting in the phenanthrene derivative **21a** in excellent isolated yields (entries 6 and 7). Under these reaction conditions, the above-mentioned **5oa** was not observed at all.

The above results revealed that the kinetically favored ipso attack intermediates **3** might undergo thermodynamically controlled skeletal rearrangement to afford the final tetrasubstituted phenanthrenes **21**. A proposed reaction mechanism is given in Scheme 4. The in situ generated 4-naphthyl 1-lithio-1,3-

SCHEME 4. Skeletal Rearrangement of the Spiro Intermediates to Form the Fused Ring Compounds



butadienes **2** solely undergo the kinetically favored ipso attack to form the lithiated dearomatized intermediates **3**, which are thermally unstable. At temperatures higher than room temperature, these intermediates **3** undergo a novel skeletal rearrangement via 1,2-alkyl shift (intermediates **22**) to afford the formally vicinal attack lithiated dearomatized intermediates **4**, which are thermally unstable and generate the stable phenanthrene derivatives via the rearomatization process.

For 4-phenyl 1-lithio-1,3-butadienes, this novel rearrangement could not happen, although at reflux of toluene, the spiro intermediates **9** gave mixtures of unknown products.

Conclusions

We have described the highly efficient and selective intramolecular nucleophilic addition of the butadienyllithium to the

aromatic rings, resulting in full dearomatization of phenyl rings and partial dearomatization of naphthyl rings via ipso attack. A wide variety of multiply substituted bicyclic and polycyclic spirocyclopentadienes and phenanthrene derivatives could be readily prepared by further treatment of the in situ generated lithiated dearomatized intermediates. Mechanistic studies revealed interesting reactivity of the ipso attack dearomatized intermediates from 4-naphthyl 1-lithio-1,3-butadienes. These ipso attack intermediates undergo a novel skeletal rearrangement via a 1,2-alkyl shift followed by rearomatization to afford the formally vicinal attack products phenanthrene derivatives.

Experimental Section

Typical Procedure for the Preparation of Spirocyclopentadiene Products 5a−n from Dearomatizing Anionic Cyclization of 4-Naphthyl 1-Lithio-1,3-butadienes Followed by Reactions with Electrophiles. To a diethyl ether (5 mL) solution of 4-naphthyl 1-iodo-1,3-butadiene **1** (0.5 mmol) at −78 °C was added *t*-BuLi (1.0 mmol, 1.5 M in pentane). The above reaction mixture was then stirred at −78 °C for 1 h. Hydrolysis of the reaction mixture of **1a** with saturated aqueous $NaHCO_3$ afforded a mixture of two products **5a** and **5a′**, which were separated using column chromatography to give pure **5a** and pure **5a′** in 69 and 21% isolated yields, respectively.

When the above reaction mixture of **1** was further treated with an electrophile (0.6 mmol) instead of being quenched with saturated aqueous $NaHCO_3$, the reaction mixture was continuously stirred at −78 °C for another 1 h and then quenched with aqueous $NaHCO_3$. The layers were separated, and the aqueous phase was extracted three times with ether. The combined extracts were washed with brine and dried over $MgSO_4$. Evaporation under reduced pressure gave a crude product **5b−n**, which was purified by flash chromatography.

5c: Colorless liquid, isolated yield 84% (160 mg); ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 0.63−0.79 (m, 6H, CH_3), 1.07−1.13 (m, 6H, CH_3), 1.82−2.04 (m, 4H, CH_2), 2.23−2.32 (m, 4H, CH_2), 2.80 (dd, J = 13.2, 9.6 Hz, 1H, CH_2), 3.27 (dd, J = 13.2, 4.8 Hz, 1H, CH_2), 3.77 (t, J = 4.5 Hz, 1H, CH), 4.98 (dd, J = 10.2, 1.5 Hz, 1H, CH), 5.80 (dd, J = 10.2, 3.6 Hz, 1H, CH), 6.58 (d, J = 7.8 Hz, 1H, CH), 6.95 (t, J = 7.2 Hz, 1H, CH), 7.10−7.31 (m, 7H, CH); ^{13}C NMR (75 MHz, $CDCl_3$, TMS) δ 14.86 (1 CH_3), 15.02 (1 CH_3), 15.12 (1 CH_3), 15.39 (1 CH_3), 18.87 (1 CH_2), 18.93 (1 CH_2), 19.16 (1 CH_2), 19.33 (1 CH_2), 40.13 (1 CH), 46.46 (1 CH_2), 62.94 (1 quart C), 125.70 (1 CH), 125.83 (1 CH), 126.02 (1 CH), 127.14 (1 CH), 127.54 (1 CH), 128.16 (2 CH), 128.24 (1 CH), 128.73 (1 CH), 129.52 (2 CH), 134.73 (1 quart C), 137.90 (1 quart C), 139.83 (1 quart C), 141.70 (1 quart C), 142.02 (1 quart C), 150.14 (1 quart C), 150.54 (1 quart C). HRMS calcd for $C_{29}H_{34}$: 382.2661, found 382.2657.

5f: Colorless liquid, isolated yield 60% (170 mg); ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 0.70−0.78 (m, 6H, CH_3), 0.86−1.00 (m, 6H, CH_3), 1.05−2.27 (m, 39H, CH_2 and CH), 5.06−5.12 (m, 2H, CH), 5.84 (dd, J = 10.2, 3.6 Hz, 1H, CH), 5.57 (dd, J = 7.8, 1.5 Hz, 1H, CH), 6.80−7.05 (m, 3H, CH); ^{13}C NMR (75 MHz, $CDCl_3$, TMS) δ 13.84 (1 CH_3), 13.99 (1 CH_3), 14.08 (2 CH_3), 23.08 (1 CH_2), 23.12 (1 CH_2), 23.14 (2 CH_2), 25.89 (3 CH_2), 26.31 (1 CH_2), 28.03 (3 CH), 32.09 (1 CH_2), 32.52 (1 CH_2), 32.55 (1 CH_2), 32.61 (1 CH_2), 36.58 (3 CH_2), 38.30 (3 CH_2), 47.21 (1 CH), 47.46 (1 quart C), 62.65 (1 quart C), 121.62 (1 CH), 126.10 (1 CH), 126.30 (1 CH), 126.96 (1 CH), 128.32 (1 CH), 131.55 (1 CH), 134.22 (1 quart C), 135.44 (1 quart C), 141.21 (1 quart C), 141.29 (1 quart C), 148.63 (1 quart C), 149.94 (1 quart C), 213.55 (1 quart C); IR (neat) ν (C═O) = 1708 cm^{-1}. HRMS calcd for $C_{41}H_{58}O$: 566.4488, found 566.4481.

5k: Colorless liquid, isolated yield 82% (160 mg); ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 0.53 (t, J = 7.5 Hz, 3H, CH_3), 0.90 (t, J = 7.5 Hz, 3H, CH_3), 1.06−1.16 (m, 6H, CH_3), 1.27 (d, J = 8.7 Hz, 1H, OH), 1.47−1.87 (m, 12H, CH_2), 2.08−2.36 (m, 6H, CH_2), 3.55 (d, J = 2.7 Hz, 1H, CH), 5.13 (dd, J = 10.2, 1.5 Hz, 1H, CH), 6.09 (dd, J = 10.5, 4.2 Hz, 1H, CH), 6.61 (dd, J = 7.8, 1.5 Hz, 1H, CH), 6.93−6.98 (m, 1H, CH), 7.04−7.09 (m, 1H, CH), 7.25−7.55 (m, 1H, CH); ^{13}C NMR (75 MHz, $CDCl_3$, TMS) δ 14.67 (1 CH_3), 14.92 (1 CH_3), 15.26 (1 CH_3), 15.73 (1 CH_3), 18.86 (1 CH_2), 18.90 (1 CH_2), 18.92 (1 CH_2), 19.39 (1 CH_2), 21.77 (1 CH_2), 22.03 (1 CH_2), 25.79 (1 CH_2), 33.69 (1 CH_2), 35.98 (1 CH_2), 49.05 (1 CH), 63.47 (1 quart C), 75.00 (1 quart C), 125.15 (1 CH), 125.54 (1 CH), 125.99 (1 CH), 127.29 (1 CH), 130.12 (1 CH), 130.85 (1 CH), 134.55 (1 quart C), 135.99 (1 quart C), 140.50 (1 quart C), 143.51 (1 quart C), 149.86 (1 quart C), 150.92 (1 quart C). HRMS calcd for $C_{28}H_{38}O$: 390.2923, found 390.2926.

5n: Colorless liquid, isolated yield 71% (127 mg); ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 0.67−0.76 (m, 6H, CH_3), 1.04−1.25 (m, 4H, CH_2), 1.64−2.06 (m, 8H, CH_2), 2.39−2.65 (m, 6H, CH_2), 3.55−3.58 (m, 1H, CH), 5.00−5.07 (m, 3H, CH_2 and CH), 5.77−5.91 (m, 1H, CH), 5.95 (dd, J = 10.2, 3.6 Hz, 1H, CH), 6.53−6.56 (m, 1H, CH), 6.90−6.95 (m, 1H, CH), 7.07−7.12 (m, 1H, CH), 7.22−7.25 (m, 1H, CH); ^{13}C NMR (75 MHz, $CDCl_3$, TMS) δ 14.43 (1 CH_3), 14.58 (1 CH_3), 22.17 (1 CH_2), 22.49 (1 CH_2), 23.84 (1 CH_2), 23.86 (1 CH_2), 24.38 (1 CH_2), 24.40 (1 CH_2), 28.57 (1 CH_2), 28.66 (1 CH_2), 37.87 (1 CH), 43.80 (1 CH_2), 63.34 (1 quart C), 116.50 (1 CH_2), 125.50 (1 CH), 125.84 (1 CH), 126.94 (1 CH), 127.92 (1 CH), 128.02 (1 CH), 128.56 (1 CH), 134.73 (1 quart C), 136.32 (1 CH), 136.91 (1 quart C), 137.34 (1 quart C), 137.85 (1 quart C), 147.37 (1 quart C), 147.83 (1 quart C). HRMS calcd for $C_{27}H_{34}$: 358.2660, found 358.2660.

Typical Procedure for the Preparation of Spirocyclopentadiene Products 10a, 10a′, 12a−l, and 13−20 from Dearomatizing Anionic Cyclization of 4-Phenyl 1-Lithio-1,3-butadienes Followed by Reactions with Electrophiles. To a diethyl ether (5 mL) solution of 4-phenyl 1-iodo-1,3-butadiene **6** (0.5 mmol) at −78 °C was added *t*-BuLi (1.0 mmol, 1.5 M in pentane). The above reaction mixture was first stirred at −78 °C for 1 h. Hydrolysis of the reaction mixture of **6a** with saturated aqueous $NaHCO_3$ afforded **8a** in 95% isolated yield.[20] When the reaction temperature of **6** was allowed to warm up to 0 °C and kept at this temperature for 2 h, hydrolysis of the reaction mixture of **6a** with saturated aqueous $NaHCO_3$ afforded a mixture of two products **10a** and **10a′**, which could be separated using column chromatography to give pure **10a** and pure **10′** in 40 and 36% isolated yields, respectively.

After the above reaction mixture of **6** was stirred at 0 °C for 2 h, instead of being quench with saturated aqueous $NaHCO_3$, the reaction mixture was further treated with an electrophile (0.6 mmol) at 0 °C for 2 h. The reaction mixture was then quenched with aqueous $NaHCO_3$. The layers were separated, and the aqueous phase was extracted three times with ether. The combined extracts were washed with brine and dried over $MgSO_4$. Evaporation under reduced pressure gave crude products **12−20**, which were purified by flash chromatography.

10a: Colorless liquid, isolated yield 40% (48 mg); ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 1.01−1.08 (m, 12H, CH_3), 2.11−2.28 (m, 8H, CH_2), 2.32 (d, J = 1.8 Hz, 2H, CH_2), 4.84−4.87 (m, 1H, CH), 5.89−5.90 (m, 2H, CH), 5.96−6.01 (m, 1H, CH); ^{13}C NMR (75 MHz, $CDCl_3$, TMS) δ 15.08 (2 CH_3), 15.50 (2 CH_3), 18.71 (2 CH_2), 18.89 (2 CH_2), 28.02 (1 CH_2), 56.50 (1 quart C), 122.53 (1 CH), 122.80 (1 CH), 126.29 (1 CH), 129.70 (1 CH), 140.61 (2 quart C), 148.70 (2 quart C). HRMS calcd for $C_{18}H_{26}$: 242.2034, found 242.2034.

10a′: Colorless liquid, isolated yield 36% (44 mg); ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 0.99 (t, J = 7.5 Hz, 6H, CH_3), 1.05 (t, J = 7.5 Hz, 6H, CH_3), 2.12 (q, J = 7.5 Hz, 4H, CH_2), 2.23 (q, J = 7.5 Hz, 4H, CH_2), 2.73−2.76 (m, 2H, CH_2), 4.94−4.98 (m, 2H, CH), 5.87−5.92 (m, 2H, CH); ^{13}C NMR (75 MHz, $CDCl_3$, TMS) δ 15.09 (2 CH_3), 15.56 (2 CH_3), 18.96 (2 CH_2), 19.17 (2 CH_2), 25.93 (1 CH), 60.57 (1 quart C), 124.49 (2 CH), 128.43 (2 CH), 141.64 (2 quart C), 148.09 (2 quart C). HRMS calcd for $C_{18}H_{26}$: 242.2034, found 242.2034.

12k′: Colorless liquid, isolated yield 50% (106 mg); ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 0.94−1.07 (m, 12H, CH_3), 2.03−2.26 (m, 8H, CH_2), 2.48 (s, 1H, OH), 4.16−4.19 (m, 1H, CH), 5.15 (dd, J = 10.2, 2.1 Hz, 2H, CH), 5.66 (dd, J = 10.5, 2.7 Hz, 2H, CH), 7.16−7.21 (m, 2H, CH), 7.29−7.34 (m, 4H, CH), 7.59−7.62 (m, 4H, CH); ^{13}C NMR (75 MHz, $CDCl_3$, TMS) δ 14.97 (1 CH_3), 15.08 (1 CH_3), 15.69 (1 CH_3), 15.77 (1 CH_3), 18.93 (1 CH_2), 18.95 (1 CH_2), 19.05 (1 CH_2), 19.12 (1 CH_2), 43.74 (1 CH), 61.10 (1 quart C), 78.79 (1 quart C), 124.74 (2 CH), 125.87 (4 CH), 126.52 (2 CH), 128.20 (4 CH), 132.88 (2 CH), 142.52 (1 quart C), 143.06 (1 quart C), 145.89 (2 quart C), 146.24 (1 quart C), 146.86 (1 quart C). HRMS calcd for $C_{31}H_{36}O$: 424.2766, found 424.2777.

12l′: Colorless liquid, isolated yield 77% (163 mg); ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 0.85−1.26 (m, 12H, CH_3), 1.99−2.34 (m, 8H, CH_2), 3.34, (dd, J = 5.1, 2.7 Hz, 1H, CH), 4.30 (br, 1H, NH), 4.48 (d, J = 3.3 Hz, 1H, CH), 5.15−5.18 (m, 2H, CH), 5.62 (d, J = 10.5 Hz, 1H, CH), 5.92 (d, J = 9.0 Hz, 1H, CH), 6.44 (d, J = 8.4 Hz, 2H, CH), 6.58−6.63 (m, 1H, CH), 7.05 (t, J = 7.5 Hz, 2H, CH), 7.19−7.40 (m, 5H, CH); ^{13}C NMR (75 MHz, $CDCl_3$, TMS) δ 15.00 (1 CH_3), 15.13 (1 CH_3), 15.64 (1 CH_3), 16.05 (1 CH_3), 18.91 (1 CH_2), 18.95 (1 CH_2), 19.05 (1 CH_2), 19.43 (1 CH_2), 42.73 (1 CH), 60.70 (1 CH), 61.05 (1 quart C), 113.07 (2 CH), 116.98 (1 CH), 123.60 (1 CH), 126.82 (2 CH), 126.90 (1 CH), 128.18 (1 CH), 128.40 (2 CH), 129.06 (2 CH), 131.08 (1 CH), 131.93 (1 CH), 141.85 (1 quart C), 142.32 (1 quart C), 143.08 (1 quart C), 146.53 (1 quart C), 146.78 (1 quart C), 147.61 (1 quart C). HRMS calcd for $C_{31}H_{37}N$: 423.2926, found 423.2871.

17: Colorless liquid, isolated yield 70% (187 mg); ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 0.81−0.98 (m, 12H, CH_3), 1.18−1.53 (m, 16H, CH_2), 1.93−2.29 (m, 8H, CH_2), 3.30 (dd, J = 5.7, 2.7 Hz, 1H, CH), 4.26 (br, 1H, NH), 4.47 (d, J = 3.6 Hz, 1H, CH), 5.11−5.16 (m, 2H, CH), 5.60−5.64 (m, 1H, CH), 5.87−5.91 (m, 1H, CH), 6.43 (d, J = 7.8 Hz, 2H, CH), 6.62 (t, J = 7.2 Hz, 1H, CH), 7.06 (dd, J = 8.1, 7.5 Hz, 2H, CH), 7.24 (t, J = 6.9 Hz, 1H, CH), 7.31−7.42 (m, 4H, CH); ^{13}C NMR (75 MHz, $CDCl_3$, TMS) δ 13.91 (1 CH_3), 14.03 (1 CH_3), 14.05 (1 CH_3), 14.20 (1 CH_3), 23.09 (1 CH_2), 23.11 (1 CH_2), 23.32 (1 CH_2), 23.36 (1 CH_2), 25.89 (1 CH_2), 25.94 (1 CH_2), 26.03 (1 CH_2), 26.62 (1 CH_2), 32.47 (1 CH_2), 32.50 (1 CH_2), 32.88 (1 CH_2), 33.16 (1 CH_2), 42.72 (1 CH), 61.03 (1 CH), 61.19 (1 quart C), 113.23 (2 CH), 117.02 (1 CH), 123.54 (1 CH), 126.90 (2 CH), 126.92 (1 CH), 128.07 (1 CH), 128.44 (2 CH), 129.02 (2 CH), 131.45 (1 CH), 132.14 (1 CH), 141.31 (1 quart C), 141.99 (1 quart C), 142.10 (1 quart C), 145.23 (1 quart C), 145.74 (1 quart C), 147.69 (1 quart C).

19: Colorless liquid, isolated yield 57% (97 mg); ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 0.95−1.08 (m, 12H, CH_3), 1.26 (t, J = 1.5 Hz, 3H, CH_3), 1.50 (br, 1H, OH), 1.64−1.88 (m, 8H, CH_2), 1.94−2.29 (m, 8H, CH_2), 2.95−2.99 (m, 1H, CH), 5.04 (dd, J = 9.9, 2.1 Hz, 1H, CH), 5.71−5.73 (m, 1H, CH), 5.86−5.90 (m, 1H, CH); ^{13}C NMR (75 MHz, $CDCl_3$, TMS) δ 14.77 (1 CH_3), 14.96 (2 CH_3), 15.05 (1 CH_3), 17.97 (1 CH_3), 18.96 (1 CH_2), 19.00 (2 CH_2), 19.04 (1 CH_2), 23.87 (1 CH_2), 23.91 (1 CH_2), 38.20 (1 CH_2), 38.32 (1 CH_2), 46.80 (1 CH), 63.78 (1 quart C), 83.94 (1 quart C), 123.17 (1 CH), 124.80 (1 CH), 132.03 (1 CH), 136.48 (1 quart C), 142.96 (1 quart C), 143.64 (1 quart C), 145.61 (1 quart C), 146.16 (1 quart C). HRMS calcd for $C_{24}H_{36}O$: 340.2766, found 340.2758.

Typical Procedure for the Preparation of Tetrasubstituted Phenanthrene Products 21a−d from 4-Naphthyl 1-Lithio-1,3-butadienes. To a mixed solvent of diethyl ether (2.5 mL) and toluene (2.5 mL) or a toluene solution of 4-naphthyl 1-iodo-1,3-butadiene **1** (0.5 mmol) at −78 °C was added *t*-BuLi (1.0 mmol, 1.5 M in pentane). After being stirred at −78 °C for 1 h, the above reaction mixture was heated up to 75 °C and kept at this temperature for 3 h. The reaction was then cooled down to room temperature and was quenched with saturated aqueous $NaHCO_3$. The layers were separated, and the aqueous phase was extracted three times with ether. The combined extracts were washed with brine and dried over $MgSO_4$. Evaporation under reduced pressure followed by flash chromatography afforded the title product. In the case of the mixed solvent of diethyl ether (2.5 mL) and toluene (2.5 mL), tetrasubstituted phenanthrene products **21a−d** were obtained as the only products. In the case of toluene as the solvent, in addition to **21a−d**, spirocyclopentadienes **5oa−c** were also obtained. The tetrasubstituted phenanthrene product **21** and the spirocyclopentadiene **5o** could be readily separated by column chromatography.

21a: Colorless liquid, isolated yield 91% (132 mg); ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 1.21−1.28 (m, 6H, CH_3), 1.34 (t, J = 7.5 Hz, 3H, CH_3), 1.64 (t, J = 7.2 Hz, 3H, CH_3), 2.92 (q, J = 7.5 Hz, 2H, CH_2), 3.00 (q, J = 7.5 Hz, 2H, CH_2), 3.13 (q, J = 7.5 Hz, 2H, CH_2), 3.33−3.35 (m, 2H, CH_2), 7.49−7.52 (m, 2H, CH), 7.61 (d, J = 9.0 Hz, 1H, CH), 7.81−7.84 (m, 1H, CH), 7.92 (d, J = 9.0 Hz, 1H, CH), 8.62−8.65 (m, 1H, CH); ^{13}C NMR (75 MHz, $CDCl_3$, TMS) δ 15.86 (1 CH_3), 15.88 (1 CH_3), 16.10 (1 CH_3), 16.31 (1 CH_3), 22.29 (1 CH_2), 22.53 (1 CH_2), 22.72 (1 CH_2), 25.27 (1 CH_2), 123.33 (1 CH), 124.60 (1 CH), 125.33 (1 CH), 125.92 (1 CH), 127.75 (1 CH), 128.02 (1 CH), 129.80 (1 quart C), 130.14 (1 quart C), 131.07 (1 quart C), 132.86 (1 quart C), 136.07 (1 quart C), 136.66 (1 quart C), 138.69 (1 quart C), 140.73 (1 quart C). HRMS calcd for $C_{22}H_{26}$: 290.2034, found 290.2038.

21d: Colorless liquid, isolated yield 90% (142 mg); ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 1.08−1.20 (m, 6H, CH_3), 1.62−2.07 (m, 8H, CH_2), 2.96−3.17 (m, 8H, CH_2), 7.48−7.51 (m, 2H, CH), 7.58 (d, J = 9.0 Hz, 1H, CH), 7.80−7.83 (m, 1H, CH), 7.88 (d, J = 9.0 Hz, 1H, CH), 8.46 (t, J = 6.3 Hz, 1H, CH); ^{13}C NMR (75 MHz, $CDCl_3$, TMS) δ 14.30 (1 CH_3), 14.83 (1 CH_3), 22.66 (1 CH_2), 22.99 (1 CH_2), 23.22 (1 CH_2), 23.76 (1 CH_2), 27.66 (1 CH_2), 27.70 (1 CH_2), 30.75 (1 CH_2), 34.71 (1 CH_2), 123.17 (1 CH), 124.56 (1 CH), 125.34 (1 CH), 125.78 (1 CH), 127.79 (1 CH), 127.92 (1 CH), 129.34 (1 quart C), 129.57 (1 quart C), 131.12 (1 quart C), 132.88 (1 quart C), 134.17 (1 quart C), 134.50 (1 quart C), 135.38 (1 quart C), 136.41 (1 quart C). HRMS calcd for $C_{24}H_{28}$: 316.2191, found 316.2200.

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Supporting Information Available: General experimental procedures, characterization data for all new starting materials and products except illustrative examples, copies of ^{1}H and ^{13}C NMR spectra for all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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