Lithium Dialkylamide Induced 1,4-Elimination of Methyl *o*-Methylbenzyl Ethers: Formation and Reactions of *o*-Xylylenes

Theodore Tuschka, Katsuyuki Naito, and Bruce Rickborn*

Department of Chemistry, University of California, Santa Barbara, California 93106

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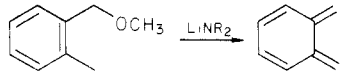
Lithium dialkylamide induced 1,4-elimination is shown to be a general reaction of methyl *o*-methylbenzyl ethers, giving *o*-xylylenes as reactive intermediates. The fate of the intermediate depends on a variety of factors including the base used, the dienophile employed as solvent, or the presence of a suitably located double bond in the substrate. With lithium diisopropylamide (LDA), a significant reaction forms the amine derived from 1,4-addition to *o*-xylylene. The use of lithium tetramethylpiperidide (LTMP) avoids this addition and allows the study of in situ generated *o*-xylylene in intermolecular Diels–Alder reactions with simple olefins, where dimerization/polymerization is the major competing pathway. Yields of Diels–Alder adducts range from negligible (cyclohexene) to high (norbornene), with 1-hexene, isoprene, and cyclopentene giving intermediate values. Intramolecular Diels–Alder reactions to form six- and five-membered rings proceed well but are not observed for the lower homologue. Second-order rate constants have been obtained for the elimination reaction of some of the substrate ethers, and the effects of structure and temperature on yields of cycloadduct are examined. LTMP is about twice as reactive as LDA in these 1,4-eliminations.

In an extensive study of the reactions of allylic ethers with dialkylamide bases, the generality of 1,4-elimination has been established.[1] Among other features, this elimination reaction exhibits preference for proton abstraction from least substituted carbon and preferred cisoid regioselectivity. The relative ease with which compounds of appropriate geometry undergo the elimination led us to examine the possibility of disrupting benzene aromaticity under these conditions. We have reported[2] the application of this method to provide an ambient-temperature synthesis of isobenzofuran and have subsequently shown[3] that 1-alkoxyisobenzofurans can be prepared, as reactive intermediates, in analogous manner. In these systems, the widely used lithium diisopropylamide (LDA) serves well as the strong base.

In this paper we describe an extension of this approach to the formation of the very reactive *o*-xylylene (**2**), i.e.

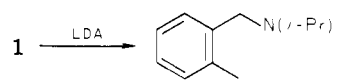


1 **2**

o-Xylylene chemistry has a venerable history, with origins in the iodide-induced ring closure of tetrabromo-*o*-xylene reported by Finkelstein,[3] leading to the pioneering work of Cava,[5] who first recognized the significance of **2** as a reactive intermediate. Recently, substituted derivatives of **2** have found wide use in synthesis, notably illustrated by the work of Kametani,[6] Oppolzer,[7] Vollhardt,[8] and others.[9-16] Thermal cleavage of benzocyclobutenes[6,7] and extrusions of sulfones[5,7] appear to be the most widely applied methods of generating *o*-xylylenes, although photoenolization[16] and thermolysis of halides[10,18] find use in certain applications. Alternatively, base-induced 1,4-eliminations of *o*-xylene derivatives have been employed. Perhaps the clearest examples of this approach are found in the work of Errede,[19] who used essentially Hofmann elimination conditions (flow tube, 200–250 °C) to generate the parent **2** (leaving group trimethylamine, base OH^-), and the recent synthetically useful (ambient temperature, again trimethylamine leaving group) application of fluoride-induced silane cleavage to give **2** and some substituted analogues.[12,13] We are aware of only a single example in the literature that may be viewed as a 1,4-elimination involving an ether (alkoxide leaving group) leading to **2**; Mann and Stewart[20] proposed the intermediacy of **2** when *o*-(methoxymethyl)benzyl chloride was treated with magnesium. Other more conventional leaving groups, e.g., halide, are expected to give nucleophilic displacement products with simple bases. Of particular interest to the present study, the use of nonnucleophilic strong base has been examined for both *o*-methyl- and *p*-methylbenzyl chloride by Olofson and Dougherty,[21] who found evidence for only α elimination to yield carbene intermediates when lithium tetramethylpiperidide (LTMP)[22] was employed.

Results and Discussion

When methyl *o*-methylbenzyl ether (**1**) is treated with LDA at room temperature or at reflux in ether/hexane, a reaction occurs that leads to product in which the amine has formally displaced the methoxy group. Similar results



(1) Unpublished work of B. H. Williams, K. Blonski, D. Svedberg, and B. Rickborn; portions of this work have been presented at the Pacific Conference on Chemistry and Spectroscopy, Pasadena, CA, Oct 1979.
(2) Naito, K.; Rickborn, B. *J. Org. Chem.* **1980**, *45*, 4061.
(3) Makhlouf, M. A.; Rickborn, B. *J. Org. Chem.* **1981**, *46*, 2734.
(4) Finkelstein, H. *Chem. Ber.* **1910**, *43*, 1528.
(5) Cava, A. A.; Deana, A. A. *J. Am. Chem. Soc.* **1959**, *81*, 4266. Cava, M. P.; Deana, A. A.; Muth, K. *Ibid.* **1959**, *81*, 6458.
(6) For a recent example, see Kametani, T.; Tsubuki, M.; Nemoto, H. *J. Org. Chem.* **1980**, *45*, 4391.
(7) Oppolzer, W. *Synthesis* **1978**, 793; *Heterocycles* **1980**, *14*, 1615.
(8) Vollhardt, K. P. C. *Acc. Chem. Res.* **1977**, *10*, 1. Vollhardt, K. P. C.; Funk, R. L. *Chem. Soc. Rev.* **1980**, *9*, 41.
(9) McCullough, J. J. *Acc. Chem. Res.* **1980**, *13*, 270.
(10) Boekelheide, V.; Ewing, G. *Tetrahedron Lett.* **1978**, 4245.
(11) Nicolaou, K. C.; Barnette, W. E.; Ma, P. J. *Org. Chem.* **1980**, *45*, 1463.
(12) Ito, Y.; Nakatsuka, M.; Saegusa, T. *J. Am. Chem. Soc.* **1980**, *102*, 863. Ito, Y.; Nakatsuka, M.; Saegusa, T. *Ibid.* **1981**, *103*, 476. Ito, Y.; Yonezawa, K.; Saegusa, T. *J. Org. Chem.* **1974**, *39*, 2769.
(13) Djuric, S.; Sarkar, T.; Magnus, P. *J. Am. Chem. Soc.* **1980**, *102*, 6885.
(14) Arnold, B. J.; Sammes, P. G. *J. Chem. Soc., Chem. Commun.* **1972**, 30.
(15) Quinkert, G.; Weber, W. D.; Schwartz, U.; Duerner, G. *Angew. Chem.* **1980**, *92*, 1060. Quinkert, G.; Schwartz, U.; Stark, H.; Weber, W. D.; Baier, H.; Adam, F.; Duerner, G. *Ibid.* **1980**, *92*, 1062.
(16) Pfau, M.; Comrisson, S.; Rowe, J. E., Jr.; Heindel, N. D. *Tetrahedron* **1978**, *34*, 3469.
(17) This route to a substituted *o*-xylylene was first demonstrated by Jensen, F. R.; Coleman, W. E.; Berlin, A. J. *Tetrahedron Lett.* **1962**, 15.
(18) Morello, M. J.; Trahanovsky, W. S. *Tetrahedron Lett.* **1979**, 4435.
(19) Errede, L. A. *J. Am. Chem. Soc.* **1961**, *83*, 949.
(20) Mann, F. G.; Stewart, F. H. *J. Chem. Soc.* **1954**, 2826.
(21) Olofson, R. A.; Dougherty, C. M. *J. Am. Chem. Soc.* **1973**, *95*, 581.
(22) The propensity of LTMP to give α-proton abstraction was found in reactions of epoxides: Kissel, C. L.; Rickborn, B. *J. Org. Chem.* **1972**, *37*, 2060.

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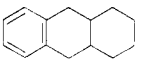
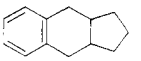
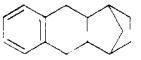
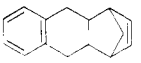
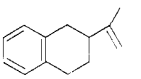
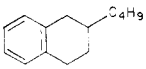
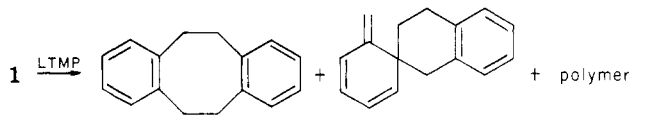
Table I. Intermolecular Diels–Alder Reaction of 2

dienophile	adduct (% yield)
cyclohexene	 (≤0.5%)
cyclopentene	 (6–20%)
norbornene	 (70%)
norbornadiene	 (56%)
isoprene	 (43%)
1-hexene	 (18%)

were observed with the *p*-methyl analogue. Although an S_N2 displacement seemed unlikely, it was ruled out by showing that methyl benzyl ether itself is recovered unchanged from the same reaction conditions. These observations suggest that 1 is converted to 2 by LDA and that the LDA/diisopropylamine adds rapidly to the reactive intermediate. Butadiene itself undergoes analogous addition reactions to give substituted *cis*-2-butenes with diethylamine/amide mixtures, and less readily with bulkier bases.[23]

In the hope of circumventing this amine addition, the use of LTMP was explored. Again facile reaction occurred, but no amine adduct was isolated. Instead, the known[19,25] dimeric products signaling the formation of *o*-xylylene were formed, along with polymer. No evidence for the for-



mation of benzocyclobutene was found. Although this is not an expected product from 2 at the temperatures employed here[24] (Roth and co-workers[25] have determined that the $\Delta H^{\ddagger}$ for the conversion of 2 to benzocyclobutene is 25.6 kcal/mol, $\Delta S^{\ddagger}$ = −5.8 cal/mol·deg, while dimer formation has $\Delta H^{\ddagger}$ of 5.3 kcal/mol, $\Delta S^{\ddagger}$ = −24.3 cal/mol·deg.), alternative mechanisms such as intramolecular S_N2 displacement of methoxide by carbanion are ruled out by this observation.

With this clear evidence that 1 forms 2 by a 1,4-elimination, and with the ability to avoid amine addition through the use of LTMP, a system was available to examine the reactions of 2 with simple olefin dienophiles. It was thought that it might be possible to generate 2 in very low concentration, and by using a large excess of dienophile (e.g., as the solvent), observe hitherto inaccessible reactions of 2 in useful yields. In other words, this approach would test the competition between the extremely rapid (but second order in 2) dimerization reaction and the pseudo-first-order Diels–Alder reactions of 2 with olefinic solvents. Activation energies for the latter processes are unknown.

As the results in Table I show, we are operating in the range of activation energies for these competitive processes where *o*-xylylene is able to discriminate between the poorer and better dienophiles. Diels–Alder adduct yields range from negligible (cyclohexene) to good (norbornene) for these intermolecular reactions.

Efforts to improve the yields of the pseudo-first-order process by very slow addition (syringe pump) of 1 to solutions of LTMP in the olefins did not materially affect the results. The overall rate-determining step is the initial 1,4-elimination leading to 2, as shown by kinetic studies discussed later, and this relative insensitivity to mode of addition of reagents is in keeping with this view of mechanism. The results show, since dimer and polymer formation were evident in cases where Diels–Alder reactions went poorly, that in spite of its great reactivity, a high enough concentration of 2 is built up to allow the presumably second-order processes to compete effectively with intermolecular Diels–Alder reactions of the poorer dienophiles.

The order of Diels–Alder reactivity reflected in the yields of adducts shown in Table I is also in keeping with expectations about dienophilicity of these simple olefins, although this property cannot be quantified and is known to vary with different dienes. Thus, simple disubstituted olefins exhibit higher activation energies, reflected in the negligible yield of adduct from cyclohexene and the modest yield from cyclopentene. At the other extreme, the notably better[26] dienophile norbornene gives adduct in high yield; as in all other known cycloaddition processes involving this olefin, reaction occurs exclusively at the exo face. Norbornadiene also gives a good yield of exo monoadduct, as demonstrated by catalytic reduction of the remaining double bond to give product identical with that formed in the norbornene reaction. The major adduct is accompanied by a small amount (ca. 2%) of isomeric (GC/MS) material that may be the endo adduct. The ^{13}C NMR spectrum of the mixture exhibits "shadow" absorptions paralleling the peaks of the major product. Norbornadiene is known[27] to be less exo selective than norbornene in cycloaddition reactions. The assignment of this minor component is tentative, and it is noted that the MS fragmentation pattern differs significantly from that of the major product. While the latter shows a base peak of 130, corresponding to retro-Diels–Alder loss of cyclopentadiene with formation of 1,4-dihydronaphthalene ion, the minor component exhibits a base peak of 105 (130 = 21%); this base peak would require a hydrogen shifted fragment from the endo cycloadduct structure.

Isoprene has found limited use as a dienophile in Diels–Alder chemistry, where it is more frequently employed as the diene component. We find that it gives reasonable yields, and considerable selectivity for cycloaddition at the least substituted olefin site, in reaction with 2. Kametani and co-workers[28] have examined the reaction of isoprene with cyano-*o*-xylylene (from thermal, 180 °C, opening of 1-cyanobenzocyclobutene) and found it to be devoid of selectivity, giving essentially equal amounts of products from both olefinic sites. Direct comparisons of the two systems are not possible because of the cyano substituent, but the selectivity observed in our study may be partly associated with the lower temperature involved.

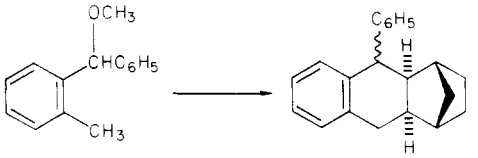
(23) Imai, N.; Narita, T.; Tsuruta, T. *Tetrahedron Lett.* **1971**, 3517.
(24) The methods of formation of benzocyclobutene via *o*-xylylene involve high-temperature generation of the intermediate; at lower temperatures the lower activation energy second-order processes such as dimer formation dominate the reactions.[25]
(25) Roth, W. R.; Biermann, M.; Dekker, H.; Jochems, R.; Mosselman, C.; Hermann, H. *Chem. Ber.* **1978**, *111*, 3892. See also: Roth, W. R.; Scholz, B. P. *Chem. Ber.* **1981**, *114*, 3741.
(26) Huisgen, R.; Ooms, P. H. J.; Mingin, M.; Allinger, N. L. *J. Am. Chem. Soc.* **1980**, *102*, 3951. Rondan, N. G.; Paddon-Row, M. N.; Caramella, P.; Houk, K. N. *Ibid.* **1981**, *103*, 2436.
(27) DeMicheli, C.; Gandolfi, R.; Oberti, R. *J. Org. Chem.* **1980**, *45*, 1209. See also ref 26.
(28) Kametani, T.; Hirai, Y.; Shiratori, Y.; Fukumoto, K.; Satoh, F. *J. Am. Chem. Soc.* **1978**, *100*, 554.

We find no more than 4% (of 47% overall yield) of product derived from cycloaddition at the more substituted double bond.

As shown in Table I, the representative monosubstituted olefin 1-hexene gives modest but significant yield of adduct. It is superior to cyclohexene but less reactive than isoprene. One other terminal olefin, not shown in the table, was also examined; although accompanied by extensive, presumably base-catalyzed, polymerization, styrene gave evidence of some cycloadduct formation. Isolation was quite difficult, involving extraction from a gelatinous reaction mixture, and the low yield (≤5%) obtained may not reflect the intrinsic activity of this olefin in Diels–Alder reaction with **2**. The adduct was characterized with use of a VPC collected sample and gave the anticipated IR, ^1H and ^{13}C NMR, and mass spectra for 2-phenyltetrahydronaphthalene.

The use of furan and *N*-methylpyrrole as potential dienophile partners with **2** was briefly examined; neither gave evidence of Diels–Alder reaction. With furan, the recovery of starting material **1** suggested that the LTMP was consumed by reaction with solvent. An attempt was also made to use phenanthrene, in ether solvent, as the trapping agent, but no volatile material of longer retention time than that of phenanthrene was observed by VPC.

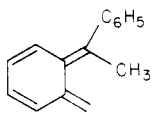
The stabilizing influence of phenyl substituents on *o*-xylylene-like materials, exemplified by 1,3-diphenylisobenzofuran, led us to examine the reactions of the ether **3**. Slow addition of **3** to a mixture of LTMP in excess norbornene/hexane gave a low yield (≤10%) of **4**, which



3 4

appeared as a single peak on VPC. No other materials in this volatility range (dimers) were observed. Preparative collection gave a colorless solid, mp 104–108 °C; in spite of these suggestions that a single product was in hand, ^1H and ^{13}C NMR showed that **4** was a near 1:1 mixture of stereoisomers. Assuming only exo face attack of norbornene, there are three reasonable explanations for formation of an epimeric mixture: (a) the presence of both *E* and *Z* forms of the phenyl-*o*-xylylene, (b) base-catalyzed isomerization of the doubly benzylic center, which probably has an effective pK_a near 33, or (c) two directions of norbornene addition to a single geometrical isomer, presumably *E*, of the reactive intermediate. Our work does not establish the preferred mechanism, but it is noted that route c has a close precedent in the formation of analogous isomers in the Diels–Alder reaction of norbornene with isobenzofuran.[3]

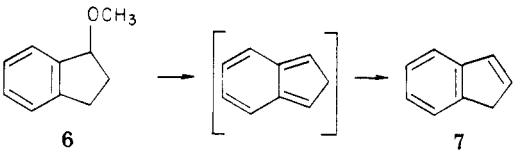
Attempts to induce electrocyclic reactions by similar treatment of **3** in cyclohexene and cyclopentene failed to give adducts. These observations are internally consistent, i.e., a low yield with norbornene suggests that little or no product will be formed with poorer dienophiles. However, the failure of the phenyl substituent to improve cycloaddition reaction is in contrast to the observation of Hornback and co-workers,[29] who obtained excellent yields of Diels–Alder adduct with cyclohexene in reaction with the *o*-xylylene **5**, generated photochemically from the corresponding styrene. Reversion to the styrene precursor



5

by facile 1,5 hydrogen shift may serve to protect **5** from alternative reactions, e.g., polymerization, which are likely competitive processes with our system.

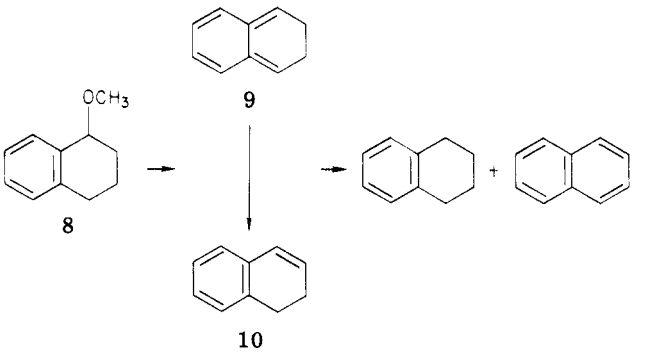
An attempt to form and trap isoindene by treatment of 1-methoxyindan (**6**) with LTMP and norbornene gave no evidence of Diels–Alder adduct formation. Instead, indene **7** was formed in high yield. While **7** could result from



6 7

1,2-elimination, our previous work[1] suggests that normally such processes are much slower than 1,4-eliminations with lithium dialkylamides. Alternatively, formation of isoindene followed by either 1,5 hydrogen shift or proton abstraction to yield the indenyl anion would lead to **7**. The sigmatropic shift (for methyl) is observed by Dolbier[30] with 2,2-dimethylisoindene, which, however, can be trapped in good yield by dimethyl maleate.

Similar treatment of methoxytetralin (**8**) with LTMP in cyclohexene gave as products tetralin and naphthalene in nearly equal amounts, with no indication of Diels–Alder reaction. Plausible intermediates are **9**, from 1,4-elimination, and/or **10**, which could be formed by any of the routes discussed for the reaction of **6**. The formation of



both tetralin and naphthalene in nearly equal amounts suggests subsequent base-catalyzed disproportionation of either **9** or **10**; an analogous reaction has been demonstrated by Schriesheim[31] when cyclohexadiene is treated with KO-*t*-Bu/Me_2SO. We note, however, that disproportionation is not a commonly observed reaction of dienes under our conditions, which allow, for example, the isolation of high yields of 1,3-cyclohexadiene from 1-methoxy-2-cyclohexene.[1]

Intramolecular Cycloadditions. The commercial availability of *o*-tolualdehyde allows facile construction, using appropriate unsaturated organometallic reagents, of the benzylic ethers needed to examine intramolecular Diels–Alder reactions of substituted *o*-xylylenes generated by treatment with strong base.

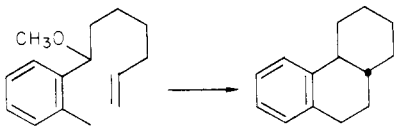
The possible modes of intramolecular cycloaddition leading to different regio- and stereochemical outcomes have been discussed by others[32] and need not be repeated

(29) Hornback, J. M.; Mawhorter, L. G.; Carlson, S. E.; Bedont, R. E. *J. Org. Chem.* **1979**, *44*, 3698.

(30) Dolbier, W. R., Jr.; Matsui, K.; Michl, J.; Horak, D. V. *J. Am. Chem. Soc.* **1977**, *99*, 3876.

(31) Hofmann, J. E.; Argabright, P. A.; Schriesheim. A. *Tetrahedron Lett.* **1964**, 1005.

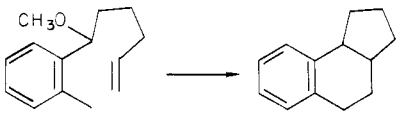
here. Such reactions involving o-xylylenes generated by other methods strongly favor the formation of the octahydrophenanthrene skeleton, as opposed to bridged structures, and our results follow this pattern. Thus, treatment of the ether **11** with LTMP affords **12**, in 71%



11 **12**

distilled yield. No isomeric materials were evident by VPC analysis of the crude product before distillation. NMR (^1H and ^{13}C) spectra of the distilled **12** indicated that it is the trans isomer shown, with no measurable (≤5%) cis product.[33] Octahydrophenanthrene has been synthesized by four other groups using variants of o-xylylene generation. Similar trans selectivity is reported by Saegusa[12] and by Funk and Vollhardt,[34] whereas Nicolaou[11] and Oppolzer[35] obtained the same major product but with measurable cis isomer formed as well. The higher temperatures employed in the latter two cases (sulfone extrusion) may account for the diminished selectivity.

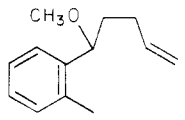
The lower homologue **13** on LTMP treatment gives **14**,



13 **14**

in somewhat lower yield (56%), and as a near 1:1 mixture of cis and trans isomers.[36] Ratios of ca. 3:1 at 300 °C[11] and ca. 2:1 at 250 °C[35] for sulfone extrusion processes have been found, although the isomer geometry has not been unambiguously established. Possible base-catalyzed equilibration has not been ruled out in the present work, preventing any firm conclusions about the effect of temperature on the stereochemistry of the electrocyclic reaction. It is worth noting, however, that the *cis*- and *trans*-hydrindan isomers differ much less in free energy than the decalins,[37] and the greater entropy of the cis isomer, as expressed in the transition states for cyclization, could lead to increases in this material with increasing temperature.

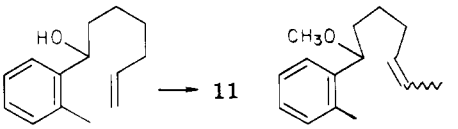
Attempts to induce elimination–cyclization of the ether **15** with LTMP resulted in loss of starting material, but



15

no evidence of volatile product formation. If the anticipated o-xylylene is formed as an intermediate, it must polymerize more readily than it undergoes cyclization.

In earlier work[1] we had found that an alternative to the standard Williamson method could be used advantageously to prepare allylic ethers. This involved dissolving the alcohol in hexamethylphosphoramide (HMPA), titrating with n-butyllithium (an orange to red color develops after the addition of 1 equiv of base), and treatment with excess methyl iodide. The ether is formed rapidly under these conditions, and workup can follow within a few minutes of adding the halide. When this procedure was applied to the alcohol **16**, a significant amount of product was found in which the terminal double bond had migrated into the chain, forming **17** along with the desired ether **11**.

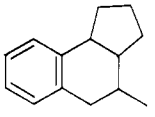


16 **17**

The usual ether-forming reaction (NaH, THF, CH_3I) with **16** gave only **11**. The HMPA procedure gave a 39:61 ratio of **11**/**17** in 70% distilled yield; ^{13}C NMR analysis of the mixture suggested that **17** was a single isomer, tentatively identified as cis on the basis of chemical shift (123.8, 130.7 ppm) comparison with the vinyl carbon values for *cis*-(123.8, 130.7) and *trans*-2-hexene (124.9, 131.8 ppm).

We briefly explored this rearrangement by treating 1-octene in HMPA containing a small amount of *tert*-butyl alcohol with n-butyllithium. Rapid rearrangement to 2-octene was observed, giving an initial trans/cis ratio of ca. 1.9/1 (by VPC). Longer reaction time led to a complex mixture of olefins, presumably by further rearrangement into the chain. The apparent specificity exhibited by **16** in this rearrangement must be attributed to the preferred geometry of intramolecular deprotonation–reprotonation. With longer reaction times at the alkoxide stage, the product from **16** also contains other materials, thought to be associated with further double bond migration and cis/trans isomerization due to intermolecular reaction.

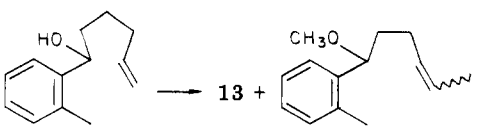
When the mixture of **11** and **17** was added to a refluxing solution of LTMP in hexane, workup and distillation gave, in 38% yield, a mixture of isomeric products exhibiting three peaks by VPC, in a ratio of 2.4:8.7:1. The first proved to be the previously characterized **12**, expected from reaction of **11**. The other two were poorly resolved by VPC but shown to be isomeric by GC/MS and are presumed to be diastereomers (cis and trans ring fused?) of the general structure **18**. The major peak was isolated by



18

preparative VPC and exhibits a methyl doublet, J = 6 Hz, by NMR that accords with this structure.

Similar treatment of the alcohol **19** in HMPA gave a mixture of ether **13** and rearrangement product **20**; the ^{13}C



19 **20**

NMR vinyl carbon shifts are 124.3 and 130.5 ppm, again suggesting the cis structure but with lesser agreement than for **17**. Subjecting this mixture to the LTMP elimination

(32) See ref 7, 8 and House, H. O.; Cronin, T. H. *J. Org. Chem.* **1965**, *30*, 1061.

(33) Professor K. P. C. Vollhardt of University of California, Berkeley kindly provided reference samples and spectra for **12** and its cis isomer.

(34) Funk, R. L.; Vollhardt, K. P. C. *J. Am. Chem. Soc.* **1976**, *98*, 6755.

(35) Oppolzer, W.; Roberts, D. A.; Bird, T. G. C. *Helv. Chim. Acta* **1979**, *62*, 2011.

(36) Professor Oppolzer kindly provided a copy of the ^{13}C NMR spectrum of the mixture of cis/trans isomers obtained in his sulfone extrusion work.[35] Line positions were identical with those of our product **14**, with intensity differences reflecting the different isomeric ratios involved.

(37) For a useful discussion of hydrindan and Decalin isomer energies, see: Eliel, E. L. "Conformational Analysis"; Wiley: New York, 1965.

Table II. Rate Constants for $LiNR_2$-Induced 1,4-Eliminations[a]

ether	base	T, °C	10^5k, M^{-1} s^{-1}	$\Delta H^{\ddagger}$ [b]	$\Delta S^{\ddagger}$ [b]	adduct, %
1	LTMP	4	39.6 ± 0.6	15	−19	23
		25	292 ± 45			14
	LDA	24	103 ± 3			23[c]
11	LTMP	22	0.98 ± 0.07	16	−26	36
		42	4.15 ± 0.23			84
		95	663 ± 99			89
	LDA	48	3.61 ± 0.21	16	−29	95
		91	76.9 ± 3			71
13	LTMP	22	5.59 ± 0.3	18	−20	36
		44	8.6 ± 0.5			40
		68	52.3 ± 3			60
		95	490 ± 230			47
	LDA	44	3.84 ± 0.19	13	−38	58
		91	61.3 ± 6.4			28
15	LTMP	71	69.6 ± 2.3	16	−27	0
		110	902 ± 62			0
	LDA	47	9.37 ± 0.27	13	−37	0
		72	42.5 ± 1			

[a] Cyclopentene was used as solvent and dienophile for ether 1. Reactions of 11, 13, and 15 were done in hexane, except for the higher temperatures where toluene was used. [b] $\Delta H^{\ddagger}$ values are in kcal/mol and $\Delta S^{\ddagger}$ in cal/mol·deg, the values are subject to large errors and are considered approximate only, and no significance is attached to the differences shown. [c] The yield at 45 °C was 55%, where the reaction was too fast to determine a rate constant. In both runs diisopropylamine adduct was observed (ca. 20%).

conditions gave, as the only volatile products, the cis/trans cycloadducts **14** expected from **13**. The failure of **20** to undergo intramolecular cycloaddition is in accord with the results from **15**.

Kinetics. Earlier attempts[1] to determine rate constants for the 1,4-elimination of allylic ethers under pseudo-first-order conditions (large excess of base) gave apparent values that diminished with extent of reaction, possibly due to association phenomena or reaction with ethereal solvents. Preliminary work with the benzyl ethers indicated that these reactions were well-behaved kinetically, allowing determination of meaningful rate constants and examination of the effects of certain variables on rate. We were particularly interested in comparing the effectiveness of LDA and LTMP in these reactions. The compounds studied were the simple ether **1**, in cyclopentene solvent, and the terminal olefinic ethers **11**, **13**, and **15**, in saturated hydrocarbon solvent. The bases were used in approximately threefold excess, to assure completion of reaction. The rates of disappearance of ether substrate were followed by VPC, using a saturated hydrocarbon internal reference. The initial concentration of $LiNR_2$ was taken from the weight of amine, treated with 1 equiv of standardized *n*-butyllithium in hexane. Adventitious proton sources would be a significant source of error in this approach, reflected primarily in nonzero intercepts in a standard second-order plot, and introducing a nonstatistical error in the calculated rate constant. Nonetheless, plots based on four to a dozen data points over 3+ "half-lives" of ether showed good linearity and only modest scatter in the zero-time intercepts. The results are given in Table II.

The inferences drawn are as follows.

(a) The reactions follow the second-order kinetic expression: rate = k[ether][base], with a linear correlation coefficient typically ≥0.99. Conclusions about order in $LiNR_2$ are tentative, since the excess of base used (2.7–4.2 times the initial concentration of ether) does not allow accurate determination of this parameter.

(b) Under the conditions employed, LTMP is a more effective base than LDA, but the difference is not large, being approximately a factor of 2 in rate for all four ethers examined. The states of aggregation of the bases are unknown, and both this and inherent basicity could affect the rate.

(c) The simple ether **1** undergoes elimination at a faster rate than the substituted derivatives, while the differences among the latter are small.

(d) The (approximate) activation parameters shown in Table II are in keeping with a bimolecular elimination mechanism, but more precise determination would be required before any conclusions are drawn about distinctions in mechanism associated with changes in base or substrate.

(e) The Diels–Alder product yields in some cases improve with increasing temperature, but this trend is not uniformly followed.

In conclusion, this work demonstrates that the generality of strong base induced 1,4-eliminations of allylic ethers extends to formation of *o*-xylylene(s) from benzylic ethers. The subsequent fate of the *o*-xylylene thus generated depends on the reactivity of the dienophile (even though this is present in very large excess as solvent), the lithium dialkylamide used, and other factors associated with the structure of the ether substrate. A major competing pathway for intermolecular Diels–Alder reactions is the dimerization of *o*-xylylene; as noted previously, Roth and co-workers[25] have determined activation parameters for this process: $\Delta H^{\ddagger}$ = 5.3 kcal/mol, $\Delta S^{\ddagger}$ = −24.3 cal/mol·deg. The $\Delta H^{\ddagger}$ values for the Diels–Alder reactions we have examined are unknown, but one might assume that the $\Delta S^{\ddagger}$ values for the intermolecular reactions would fall in the usual range of −30 ± 5 cal/mol·deg.[38] Intramolecular cycloaddition reactions would be expected to have less negative $\Delta S^{\ddagger}$ values and thus benefit from increasing temperature in competition with intermolecular processes such as dimerization. The product yield data in Table II show this trend in some instances but not others, perhaps due to other intervening processes that become more important at higher temperatures.

Experimental Section

Melting points were determined on a Mel-temp apparatus in open tubes and are uncorrected. Routine ^1H NMR spectra were obtained on a Varian T-60 instrument using CCl_4 solvent, ^{13}C NMR spectra were obtained on a Varian CFT-20 instrument, and chemical shift values are reported relative to $CDCl_3$ solvent at

(38) See: Lowry, T. H.; Richardson, K. S. "Mechanism and Theory in Organic Chemistry", 2nd ed.; Harper and Row: New York, 1981; p 848.

76.9 ppm. All reactions were carried out under nitrogen. Slow additions were accomplished with either a Sage 341-A syringe pump or a simpler device that we have dubbed a "clockdrive"; a 110-V synchronous clock motor was fitted with a 1.8 cm diameter pulley, to which was fastened a string holding a 1.1-kg metal block. The weight was balanced on the top of a vertically clamped 1.2 cm inner diameter syringe, giving a delivery rate of 0.84 mL/h. High-resolution MS were obtained on an AEI MS-902 instrument, and GC/MS spectra were provided by Dr. Robert Petty of the UCSB Marine Science Institute, using an HP 5992-A instrument, with 70-eV ionizing voltage. VPC analyses were done on a HP 5750 temperature-programmed instrument, using in most instances a 5% Apiezon N column. Preparative collections were carried out on a Varian 200 instrument using a 0.25 in. 10% Apiezon N column. Combustion analyses were performed by Galbraith Laboratories, Knoxville, TN.

Methyl 2-Methylbenzyl Ether (1). Lithium aluminum hydride reduction of methyl 2-methylbenzoate gave the alcohol, which was converted to the methyl ether 1 by dissolving in HMPA, titrating to a yellow-orange color with *n*-butyllithium in hexane, and immediate treatment with twofold excess methyl iodide. After being stirred for 20 min at room temperature, the mixture was poured into water, and extracted with pentane. Drying, evaporation, and distillation gave 1 in 90% yield, bp 50 °C (3 torr) [lit.[39] bp 86–87 °C (20 torr)]; spectral data agree with those reported,[39] and purity was established by VPC.

Diels–Alder Reactions. General Procedure. For preparative-scale reactions, the LTMP solutions were formed by adding distilled tetramethylpiperidine (5.0 mL) to 17.0 mL of 1.6 M *n*-butyllithium in hexane; the base was used either in this solution, or the hexane vacuum evaporated to replace solvent. The olefin solvent was added (excess, usually 10 mL for the simple materials) along with a weighed amount of a suitable internal standard hydrocarbon, e.g., tridecane. In general, the mixtures were brought to reflux, and 1 (2.0 g dissolved in an additional 10 mL of olefin) was added by syringe pump. After addition, refluxing was continued an additional 10–20 h. The reaction mixtures were quenched by addition of water, and the organic phase was analyzed and/or separated by VPC.

Cyclopentene. Numerous runs were made with this olefin, varying time and temperature, giving yields of Diels–Alder adduct ranging from 6% to 20%: ^{1}H NMR 0.8–3.0 (m, 12 H), 6.8–7.2 ppm (m, 4 H); GC/MS 172 (48), 143 (12), 129 (40), 115 (26), 104 (100), 91 (16); MS 172.1253 (calcd 172.1252). Other volatile products isolated were the Diels–Alder dimer of *o*-xylylene (at shorter times and lower temperatures) and dibenzocyclooctadiene, identified by comparison with literature descriptions;[19] polymeric material was also formed.

Cyclohexene. The general procedure applied to cyclohexene in several runs gave only traces (<1%) of presumed Diels–Alder adduct, identified by GC/MS only: 186 (32), 142 (31), 128 (34), 115 (36), 104 (100), 91 (20).

Isoprene. A solution of LTMP was prepared from 26 mL of 1.6 M *n*-butyllithium and 7.5 mL of tetramethylpiperidine. The hexane was replaced by 20 mL of isoprene and the mixture brought to reflux; 3.0 mL of 1 dissolved in an additional 20 mL of isoprene was added with use of the clockdrive apparatus. Refluxing was continued 16 h after addition was complete. On cooling, the contents were poured into water and ether and separated, and the ether phase was washed with 10% HCl (three times) and brine and dried over K_2CO_3. The solvent was evaporated and the residue distilled, giving a fraction bp 64 °C (0.11 torr), 1.8 g (47%). VPC of this material indicated a minor (8%) component, not identified but presumed to be isomeric on the basis of boiling point and VPC retention time, followed by the major product which was collected: ^{1}H NMR 1.8 (s, 3 H), 1.8–2.5 (m, 3 H), 2.5–3.0 (m, 4 H), 4.6 (br s, 2 H), 6.9 ppm (br s, 4 H); ^{13}C NMR 20.7, 28.31, 29.55, 35.0, 41.8, 109.2, 125.5 (2 C), 128.8, 129.0, 136, 136.3, 149.0 ppm; MS: 172 (16), 157 (10), 129 (100), 104 (36), 91 (14).

Styrene. Freshly distilled styrene was used, and the reaction was run at room temperature; after 24 h it had turned into a viscous orange semisolid. Water and ether were added, and the organic phase was filtered through glass wool. Evaporation and preparative VPC collection gave the adduct,[40] in low yield as estimated by peak size vs. volume of injection. ^{1}H NMR 2.1 (m, 2 H), 3.0 (m, 5 H), 6.9 (br s, 4 H), 7.2 ppm (s, 5 H); ^{13}C NMR 29.7, 30.3, 37.6, 40.7, 125.5, 125.6, 126.1, 126.8 (2 C), 128.4 (2 C), 128.80, 128.82, 128.9, 136.0, 137.0, 146.5; MS 208 (22), 193 (13), 130 (44), 115 (28), 104 (100), 91 (32); MS 208.127 (calcd 208.125).

1-Hexene. This reaction was carried out at reflux in a 60:40 mixture of 1-hexene/hexane, with 24 h of refluxing after slow addition of 2.4 g of 1. Distillation, bp 74–79 °C (0.05 torr), gave 0.6 g (18%) of material,[41] which was further purified by preparative VPC collection: ^{1}H NMR 0.8–1.1 (s, 4 H), 1.3–1.6 (m, 9 H), 2.3–3.0 (m, 4 H), 7.0 (s, 4 H); ^{13}C NMR 14.0, 22.9, 29.2 (2 C), 29.6, 34.2, 36.3 (2 C), 125.3 (2 C), 128.7, 129.0, 136.9, 140.0; MS 188 (45), 130 (69), 117 (74), 104 (100), 91 (98), 78 (59); MS 188.155 (calcd 188.156).

Norbornene. A mixture of 20 g of norbornene and excess LTMP in hexane (40 mL) was refluxed, while 5.0 g of 1 diluted to 10 mL with hexane was added over a period of 6 h. After brief additional heating, the mixture was cooled and washed with 10% HCl and then water, after which the organic phase was dried and rotary evaporated. Distillation at atmospheric pressure to remove the excess norbornene was followed by distillation at 0.05 torr, where the product, 5.1 g (71%), boiled at 91–93 °C. Further analysis was done on material collected by VPC, with mp 69–71 °C: ^{1}H NMR 0.9–3.0 (m, 14 H), 7.0 ppm (s, 4 H); ^{1}H NMR (360 MHz) 0.95 (dt, 1 H, J = 10.2, 1.4 Hz), 1.07 (dd, 2 H, J = 7.2, 2.2 Hz), 1.42–1.49 (m, 4 H), 1.57 (dt, 1 H, J = 10.2, 2,2 Hz), 1.86–1.88 (m, 2 H), 2.07 (dd, 2 H, J = 13.8, 11.4 Hz), 2.46 (dd, 2 H, J = 13.8, 5.8 Hz), 7.04–7.4 ppm (m, 4 H); ^{13}C NMR 29.6, 33.2, 33.5, 42.7, 43.8, 125.8, 126.7, 139.2 ppm; MS 198.138 (calcd 198.141), 198 (100), 155 (10), 130 (40). Anal. Calcd for $C_{15}H_{18}$: C, 90.6; H, 9.15. Found: C, 90.6; H, 9.28.

Norbornadiene. This reaction was carried out as described for norbornene but at 50 °C with heating continued for 20 h after slow addition. Distillation gave 4.0 g (56%) of material with bp 88 °C (0.05 torr). VPC analysis showed two peaks in a ratio of 96:4. The major peak was collected and had the following: mp 56–60 °C; ^{1}H NMR 1.0–3.1 (m, 10 H), 6.0–6.2 (m, 2 H), 7.0 ppm (s, 4 H); MS 196.129 (calcd 196.125), 196 (5), 130 (100), 115 (39), 77 (14); ^{13}C NMR 34.9, 40.3, 42.3, 47.3, 125.7, 126.7, 136.8, 139.7 ppm. The minor product by GC/MS had peaks at 196 (15), 181 (16), 167 (11), 130 (22), 115 (35), 105 (100), 91 (30).

A sample of the major product was hydrogenated in ethanol with Adams' catalyst, taking up 1 equiv of hydrogen. The reduced material was identical with the adduct from norbornene by melting point (66–68 °C), mixture melting point (67–70 °C), and IR.

2-Methyl-1-(methoxyphenylmethyl)benzene (3). Phenylmagnesium bromide was prepared in the usual way from 28.5 g of bromobenzene and 4.0 g of magnesium, in ether. This solution was cooled to 0 °C, and 20.0 g of *o*-tolualdehyde was added dropwise, followed by stirring an additional hour. Saturated ammonium chloride (100 mL) was added to quench the mixture, which was then clarified by filtration through glass wool. The organic phase was washed with brine, dried over K_2CO_3, and evaporated to give 21.0 g (64%) of yellow viscous oil from which pale-yellow crystals, mp 76–80 °C, separated on standing: ^{1}H NMR 2.2 (s, 3 H), 5.8 (s, 1 H), 7.0–7.5 ppm (m, 9 H).

This alcohol was converted to the methyl ether by using a threefold excess of NaH (hexane washed) and a fourfold excess of methyl iodide in THF with overnight stirring. The excess hydride was quenched by slow addition of brine, and the organic phase was dried and vacuum evaporated. Distillation gave 17.0 g (76%) of 3 with the following: bp 94–97 °C (0.1 torr); ^{1}H NMR 2.2 (s, 3 H), 3.2 (s, 3 H), 5.3 (s, 1 H), 7.0–7.5 ppm (m, 9 H).

Reaction of 3 with Norbornene. A solution of LTMP was prepared by adding 2.5 mL of tetramethylpiperidine to 9.0 mL of 1.6 M *n*-butyllithium in hexane, and 14.0 g of norbornene in an additional 10 mL of hexane was added. The ether 3, 1.0 g in 10 mL of hexane, was added over a period of 6 h at room temperature, and stirring was continued an additional 18 h. No

(39) Maycock, A. L.; Berchtold, G. A. *J. Org. Chem.* **1970**, *35*, 2532.

(40) Gutsche, C. D.; Jason, E. F.; Coffee, H. E. *J. Am. Chem. Soc.* **1958**, *80*, 5756.

(41) Bailey, A. S.; Smith, J. C.; Staveley, C. M. *J. Chem. Soc.* **1956**, 2731.

internal standard was used in this reaction, but the yield of adduct was estimated to be poor (≤10%) by VPC. A single long retention time peak (15 min, 2-ft SE-30, 220 °C) was observed and this material was collected for analysis: mp 104–108 °C; ^{1}H NMR 0.5–3.0 (m, 12 H), 3.4 (d, ca. 0.5 H, J = 10 Hz), 4.2 (d, ca. 0.5 H, J = 6 Hz), 6.5–7.8 ppm (m, 9 H); ^{13}C NMR 142.1, 142.0, 141.5, 140.2, 139.3, 139.7, 130.1, 129.6, 128.4, 127.7, 127.5, 127.3, 126.6, 126.4, 126.1, 125.8, 50.4, 48.2, 47.8, 44.6, 43.9, 43.0, 42.8, 40.8, 39.5, 34.1, 33.7, 33.2, 30.7, 30.1, 29.7, 29.5 ppm; MS 274 (67), 205 (22), 196 (29), 183 (19). Anal. Calcd for $C_{21}H_{22}$: C, 92.0; H, 7.98. Found: C, 91.9; H, 8.08.

Attempted reaction of **3** in cyclohexene at room temperature gave no volatile material but gave instead a tan, insoluble solid, apparently polymeric. Similar behavior occurred in cyclopentene, where traces of volatile material were observed by VPC but not characterized.

1-Methoxyindan (6) with LTMP. Reduction of 1-indanone with lithium aluminum hydride gave 1-indanol, which was converted to the methyl ether by the HMPA procedure described earlier. Distillation gave **6** in 41% yield: bp 59–61 °C (1.1 torr); ^{1}H NMR 2.0–3.1 (m, 4 H), 3.3 (s, 3 H), 4.6–4.9 (app t, 1 H), 7.1–7.4 (m, 4 H). The ether (1.0 g) was added to excess LTMP in hexane containing a large excess of norbornene, and the mixture was kept at 60 °C for 18 h. VPC analysis, using tetradecane as the internal standard, indicated the formation of indene only, in 81% yield. A sample was collected and the structure verified by comparison of known spectra.

1,2,3,4-Tetrahydro-1-methoxynaphthalene (8) with LTMP. Reduction of 3,4-dihydro-1(2*H*)-naphthalenone and conversion of the crude alcohol to the ether was accomplished as described above. The product **8** was obtained in 65% yield on distillation: bp 63–65 °C (0.1 torr); ^{1}H NMR 1.8–2.0 (m, 4 H), 2.5–2.8 (m, 2 H), 3.3 (s, 3 H), 4.0–4.3 (m, 1 H), 6.8–7.4 (m, 4 H). The reaction of **8** with excess LiTMP and norbornene was carried out at room temperature for 24 h. VPC analysis indicated the loss of starting material and the formation of two volatile products in approximately equal amounts. These were individually collected and shown by spectral comparison to be naphthalene and tetralin. A related disproportionation of 1,4-dihydronaphthalene with KO-*t*-Bu/Me_2SO has been reported.[42]

1,2,6-Tribromohexane. Caution: Following the procedure in "Organic Syntheses",[43] using PBr_3 and 1.5 mol of 1,2,6-hexanetriol, vigorous reaction, flames, and expulsion of material occurred when the mixture was brought to reflux. Similar behavior has been noted previously.[44] The tribromide was obtained in 39% yield, bp 107–114 °C (1.5 torr).

2-Methyl-1-(1-methoxy-6-heptenyl)benzene (11). The tribromide (70 g) was used directly to prepare 5-hexenylmagnesium bromide as described previously.[45] When it was judged that formation of the Grignard reagent was complete, 25.0 g of *o*-tolualdehyde was added dropwise at 0 °C, and stirring was continued overnight. The usual workup and distillation gave 10 g of recovered aldehyde and 19 g (46%) of the desired alcohol, bp 122–126 °C (1.0 torr). This material had ^{1}H and ^{13}C NMR spectra as anticipated and was used to prepare the methyl ether by the NaH/THF/CH_3I procedure; distillation gave 80% of **11**: bp 84–87 °C (0.1 torr); ^{1}H NMR 1.1–2.2 (m, 8 H), 2.3 (s, 3 H), 3.1 (s, 3 H), 4.2–4.5 (m, 1 H), 4.8–5.1 (m, 2 H), 5.3–6.1 (m, 1 H), 6.9–7.5 (m, 4 H); ^{13}C NMR 19.0, 25.7, 29.1, 33.9, 37.4, 56.2, 80.7, 114.4, 126.1, 126.3, 127.0, 130.5, 134.9, 138.7, 140.8. Anal. Calcd for $C_{15}H_{22}O$: C, 82.5; H, 10.15. Found: C, 82.7; H, 9.98.

1,2,3,4,4a,9,10,10a-Octahydrophenanthrene (12). A solution of LTMP (0.06 mol) in 50 mL of hexane was brought to reflux, and 3.7 g (0.017 mol) of **11** was added dropwise. After 8 h heating was discontinued, and stirring was continued overnight. The residue from the usual workup was distilled, giving 2.2 g (71%) of **12**, bp 117–120 °C (0.15 torr). The ^{1}H NMR and MS accorded with those in the literature;[46] ^{13}C NMR 32.8, 33.4, 36.3, 37.1, 37.4, 40.9, 47.1, 50.3, 81.9, 83.5, 85.0, 131.8, 135.4, 143.5, 147.0 ppm.

2-Methyl-1-(1-methoxy-5-hexenyl)benzene (13). The byproduct 1,2,5-tribromopentane from the "Organic Syntheses" preparation of tetrahydrofurfuryl bromide[47] was obtained in 15% yield, bp 96–99 °C (1.5 torr). The 5-pentenyl Grignard reagent was prepared from this tribromide and treated with *o*-tolualdehyde as described above for the higher homologue. The alcohol was obtained in 32% yield (46% based on recovered aldehyde): bp 116–117 °C (1.4 torr); ^{1}H NMR 1.4–2.3 (m, 6 H), 2.3 (s, 3 H), 3.5 (s, OH), 4.8–6.0 (m, 4 H), 7.0–7.4 ppm (m, 4 H); ^{13}C NMR 19.8, 25.2, 33.6, 37.5, 70.2, 114.6, 125.4, 126.1, 126.8, 130.2, 134.2, 138.6, 143.1 ppm.

The ether **13** was prepared by using the NaH/CH_3I method: 75% yield; bp 66–70 °C (0.05 torr); ^{1}H NMR 1.2–1.7 (m, 4 H), 1.7–2.2 (m, 2 H), 2.2 (s, 3 H), 3.1 (s, 3 H), 4.0–4.4 (m, 1 H), 4.6–5.1 (m, 2 H)e, 5.6–6.0 (m, 1 H), 6.8–7.5 ppm (m, 4 H); ^{13}C NMR 19.0, 25.5, 33.9, 37.0, 56.2, 80.6, 114.6, 126.2, 126.3, 127.0, 130.5, 134.9, 138.7, 140.8. Anal. Calcd for $C_{14}H_{20}O$: C, 82.3; H, 9.87. Found: C, 82.5; H, 9.71.

2,3,3a,8,9,9a-Hexahydro-1*H*-benz[*e*]indene (14). To a threefold excess of LTMP in refluxing hexane containing a weighed amount of internal standard tetradecane, the ether **13** (0.89 g) was added dropwise. After 4 h the starting material had been consumed, and two volatile products were formed in essentially equal amounts, in overall 56% yield. The two VPC peaks, which had very similar retention times, were collected together for further analysis: ^{1}H NMR 0.9–3.1 (m, 12 H), 7.0 ppm (s, 4 H); ^{13}C NMR[36] 22.7, 24.5, 27.5, 28.2, 28.6, 29.3, 30.1, 30.8, 32.5, 35.2, 37.4, 42.7, 44.0, 47.6, 125.1, 125.3, 125.5, 125.8, 126.0, 128.4, 129.1 ppm; MS 172 (50), 144 (59), 143 (49), 129 (100).

2-Methyl-1-(1-methoxy-4-pentenyl)benzene (15). The Grignard reagent was prepared in the usual way from commercial 4-bromo-1-butene and treated with *o*-tolualdehyde. The alcohol had bp 103–106 °C (1.5 torr) and was obtained in 36% yield. Conversion to the ether as above gave 71% of **15**: bp 66–72 °C (1.0 torr); ^{1}H NMR ($CDCl_3$) 1.4–2.4 (m, 4 H), 2.4 (s, 3 H), 3.2 (s, 3 H), 4.2–4.6 (t, 1 H), 4.8–5.2 (br t, 2 H), 5.4–6.1 (m, 1 H), 7.0–7.5 ppm (m, 4 H). Treatment of **15** with LTMP gave no evidence of volatile product by VPC analysis.

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