Zeolite β Induced Rearrangement of Allyl Benzyl Ethers. 6. Variation of the Aromatic Part and Synthesis of Dihydronaphthalene Derivatives†

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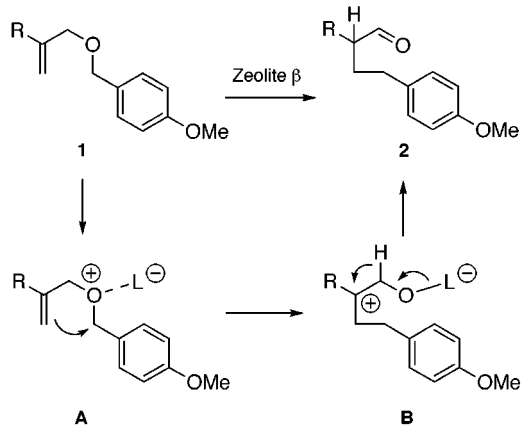
Received April 15, 1998

The zeolite β induced rearrangement of substituted allyl benzyl ethers to give 4-arylbutanals was investigated with respect to the substituents in the aromatic ring. In some cases the resulting aldehydes cyclized spontaneously to give dihydronaphthalene derivatives. The rearrangement and also the ring closure to dihydronaphthalenes failed or gave poor yields in cases where too weak electron-donating substituents were present in the aromatic ring. Also the dimensions of the pore size of the zeolite in relation to the transition state of the cyclization seemed to be of importance. Replacement of the benzylic part with other structures potentially capable of stabilizing cationic centers have hitherto not resulted in successful rearrangements.

Introduction

We recently found that substituted alkoxybenzyl allyl ethers **1** rearranged to give 4-arylbutanals **2** on treatment with zeolite β or $BF_3{\cdot}OEt_2$ via a combined 1,4-rearrangement/1,2-migration sequence (Scheme 1).[1] Here the overall reaction is referred to as the BenzAll rearrangement (benzyl allyl ether rearrangement). As an early example, a natural product was synthesized very efficiently using this rearrangement as a key step,[2] and we have also reported on the mechanism,[3] the reaction conditions,[4] and variations of the allylic moiety.[5] We now present results for substrates carrying other aromatic parts than *p*-methoxyphenyl as part of an ongoing study of the scope and limitations of the BenzAll rearrangement.

Scheme 1. **L = $BF_3{\cdot}OEt_2$ or Zeolite β**



Results and Discussion

The reactions were performed in a very simple and practical way. Mixtures of the substrates **1** and zeolite β in dichloromethane were stirred at +20 °C for 12 h, followed by filtration and evaporation of the solvent. Thus, extraction is not necessary in contrast to methods using Lewis acids in solution. As seen in Table 1, a number of substrates rearranged to give the corresponding 4-arylbutanals and in some cases the aldehydes cyclodehydrated in situ to give dihydronaphthalenes. While the two monomethoxy-substituted substrates **1a** and **1b** carrying the methoxy substituent in the 2-position rearranged to give aldehydes **2a** and **2b** in good yields (entry 1), the 3-methoxy-substituted substrate **1q** (Figure 1), and the unsubstituted benzyl ether itself did not rearrange.[1]

Also the di- and trisubstituted methoxy derivatives shown in entries 2−8 rearranged efficiently except for the low-yielding **1e**. The aldehydes resulting from the disubstituted derivatives **1e**−**g** cyclodehydrated spontaneously in the presence of the zeolite to give the dihydronaphthalenes **2e**−**g**.[6] In the case of **1e**, the rearrangement was not as favored as one might have expected. Due to steric crowding the lone pairs of the 2-methoxy group is probably forced out of conjugation with the π-system of the phenyl ring; a case of steric inhibition of resonance.[7−9] However, as soon as some of the corresponding aldehyde was formed, it immediately cyclodehydrated to give the dihydronaphthalene **2e**. The cyclization step was of course facilitated by the presence of the 3-methoxy group. Even if the 2-methoxy group of **1i** also would be inefficient in delocalization of charge due to steric inhibition, the less-crowded 4-methoxy group could serve this purpose, thus promoting the rearrangement to give **2i** in good yield (entry 7).

† For Part 5, see ref 5.

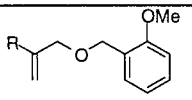
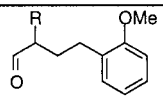
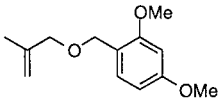
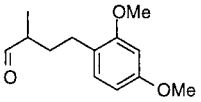
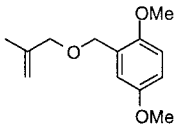
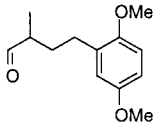
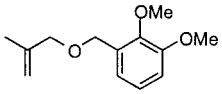
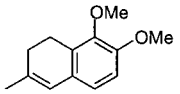
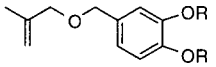
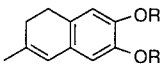
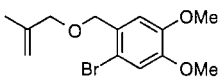
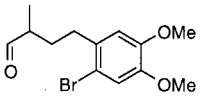
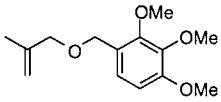
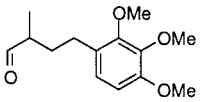
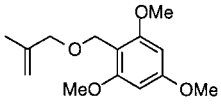
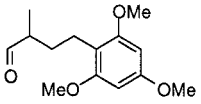
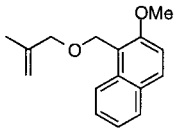
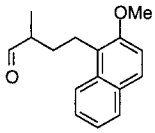
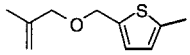
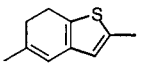
(1) Wennerberg, J.; Eklund, L.; Polla, M.; Frejd, T. *Chem. Commun.* **1997**, 445.
(2) Wennerberg, J.; Frejd, T. *Nat. Prod. Lett.* **1997**, *10*, 1−6.
(3) Wennerberg, J.; Frejd, T. *Acta Chem. Scand.* **1998**, *52*, 95−99.
(4) Wennerberg, J.; Olofsson, C.; Frejd, T. *Acta Chem. Scand.* **1998**, *52*, 232−235.
(5) Wennerberg, J.; Olofsson, C.; Frejd, T. *J. Org. Chem.* **1998**, *63*, 3595−3598.

(6) In connection with the synthesis of dihydronaphthalene derivatives, we observed that some samples were oxidized to naphthalene derivatives during storage in $CDCl_3$ solution. This is probably due to air dissolved in the solvent, since this phenomenon was not observed with neat crystalline substances, although they were still somewhat sensitive to oxygen.

(7) Wepster, B. M. *Recl. Trav. Chim. Pays-Bas* **1952**, *71*, 1159−1178.
(8) Wheland, G. W. *The Theory of Resonance*; Wiley & Sons: New York, 1944.
(9) Exner, O.; Folli, U.; Marcaccioli, S.; Vivarelli, P. *J. Chem. Soc., Perkin Trans. 2* **1983**, 757−760.

10.1021/jo980698n CCC: $18.00
Published on Web 12/12/1998

Table 1. Results of the Zeolite β Catalyzed Rearrangement of Substituted Benzyl Ethers 1a–l[a]

Entry	Start. mtrl.		Product		Yield (%)
1		**1a** R=H **1b** R=Me		**2a** R=H **2b** R=Me	69 76
2		**1c**		**2c**	71
3		**1d**		**2d**	68
4		**1e**		**2e**	11
5		**1f** R=Me **1g** R= -CH_2-		**2f** R=Me **2g** R= -CH_2-	63 61
6		**1h**		**2h**	72
7		**1i**		**2i**	75
8		**1j**		**2j**	57
9		**1k**		**2k**	62
10		**1l**		**2l**	10

[a] Conditions: 1 mmol scale, 100 mg of zeolite β, 12 h, rt.

The naphthalene derivative **1k** gave a useful yield of **2k** (entry 9) but cyclization leading to a seven-membered ring was not observed under the mild conditions used. A slow reaction of the thiophene ether **1l** was noticed at room temperature and in refluxing dichloromethane a low yield of the benzo[*b*]thiophene derivative **2l** was formed. A more detailed investigation of other thiophene cases is in progress in our laboratory. It should be mentioned that the corresponding furan derivative, **1u** (Figure 1), was too labile to give any identifiable products under the reaction conditions used.

From the results shown in Table 1 it is apparent that the rearrangement required that the positive charge (full or partial) on the benzylic carbon could be delocalized by the substituents in the aromatic ring. Thus, the methoxy groups in the 2- and 4-positions were ideally positioned for the rearrangement unless steric inhibition of resonance prevented efficient delocalization of the positive charge. Most likely this explains why **1m** had to be heated (110 °C) in order to react, but then gave rise to three compounds. The first formed aldehyde probably cyclodehydrated under these condidtions to give naphthalene derivative **2m** together with **3** and **4** in a 3:2:2 ratio, respectively (Scheme 2). The latter two compounds may have been formed via disproportionation of **2m** due to the higher reaction temperature. Steric inhibition of resonance may also explain why **1v** did not rearrange (Figure 1) and that **2i** did not cyclize (entry 7). Molecular

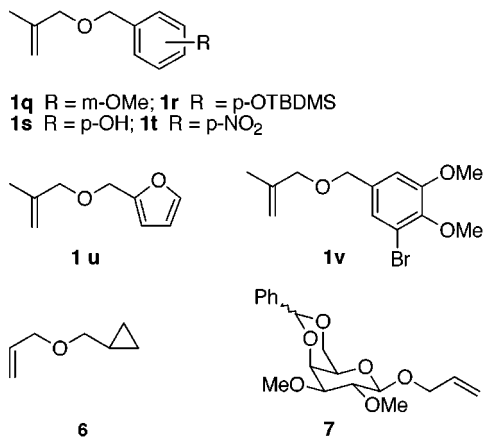
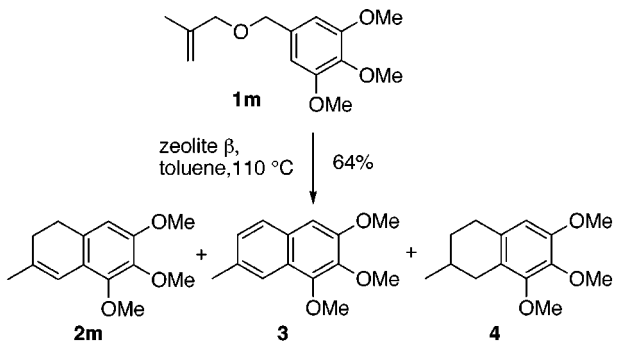


Figure 1. Examples of allylic ethers for which the BenzAll rearrangement was unsuccessful.

Scheme 2

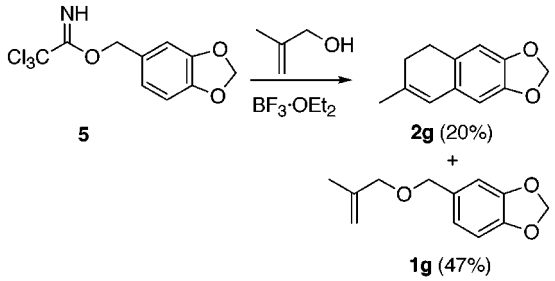


mechanics calculations (MM3(92))[10] clearly indicated that the lone pairs of the 3-methoxy group of 2,3,4-trimethoxytoluene, a model of **2i**, did not overlap with the π-system of the benzene ring in the lowest energy conformations.

The easy formation of the dihydronaphthalenes may be explained by the fact that all substrates carried a methoxy group in the 3-position in relation to the benzylic carbon. In the cyclization step this methoxy group will be positioned in the para position to the ring carbon undergoing electrophilic attack. The 2,4-dimethoxy substrate **1c** (entry 2) cannot easily undergo ring closure since both methoxy groups would be in the meta position to the cyclization site. Interestingly, the 2,5-dimethoxy compound **1d** (entry 3) and the bromo compound **1h** (entry 6) were very well arranged for a tandem rearrangement−cyclodehydration reaction, but still gave very little of the cyclization products corresponding to aldehydes **2d** and **2h**. In these cases the dimensions of the transition states leading to ring closure (estimated to be >7.8 Å for both cases) would be too large to be accommodated in the pores of the zeolite (7.4 Å). This was, however, not the case for **1f** and **1g** having the substituents in the 3- and 4-positions. Here the transition states for the cyclizations would be smaller (<7.4 Å) and would therefore better fit the size of the pores, resulting in a more efficient cyclization.[11] Soluble Lewis acids such as $BF_3{\cdot}OEt_2$ did indeed induce cyclization of **2d** as judged by NMR analysis of a purified sample, but the reaction mixture contained several other unknown compounds.

(10) Software: MacMimic. InStar Software AB, Ideon Research Park, S-223 70 Lund, Sweden.

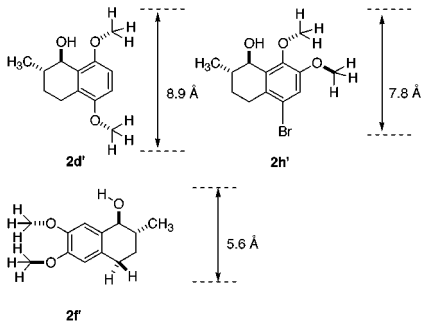
Scheme 3



However, to determine if the cyclization may take place inside the pores of the zeolite, further experimentation is necessary.

The $BF_3{\cdot}OEt_2$-catalyzed trichloroacetimidate method is frequently used for PMB-protection of alcohols[12] and was also very suitable for the synthesis of the allyl benzyl ethers used in this investigation. Since we earlier showed that besides zeolites,[13] $BF_3{\cdot}OEt_2$ also catalyzed the BenzAll rearrangement,[1,3] it occurred to us that 4-arylbutanals and perhaps also the dihydronaphthalenes could be formed in situ already in the benzylation step. When this methodology was applied to the coupling of 3,4-dimethoxybenzyl alcohol with 2-methyl-2-propenol, the dihydronaphthalene derivative **2g** was indeed formed directly in the reaction mixture (Scheme 3). Even if the reaction was rather low yielding, it still represents an example of an overall 4-step in situ production of dihydronaphthalenes from the allyl alcohol/trichloroacetimidate mixture. Attempts to increase the yield by using a higher concentration of the Lewis acid were unsuccessful due to decomposition of the imidate.

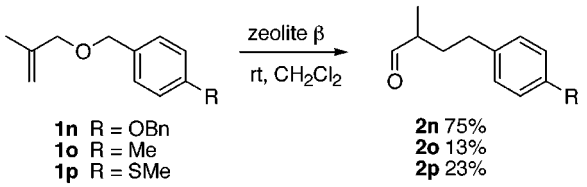
(11) We believe that the structures **2d′**, **2h′**, and **2f′** of the initial products of the carbocyclization could be used as reasonable transition-state models for estimating the sizes of the transition states of the cyclizations. Thus, these structures were used as input structures for the molecular mechanics calculations of the low-energy conformers using CS Chem3D Pro version 3.2. In the case of **2d′** the lowest energy conformation obtained was the one having the methoxy methyls essentially in plane with the aromatic ring. The distance between the atomic nulei of the outermost hydrogens of the methoxy groups was 8.9 Å. For **2h′** the corresponding treatment gave a distance between the bromine and the methyl hydrogens of the para-positioned methoxy group of 7.8 Å, and for **2f′** the smallest distance 5.6 Å was between the benzylic methylene hydrogens and the OH group. It should be pointed out that all structures occupy larger volumes when the van der Waals radii are included. Thus, for **2f′** it was estimated that the molecule would be accommodated in a pore size of 7.4 × 7.4 Å. In all three cases the trans orientation of the hydroxyl group and the methyl group of the nonaromatic ring was used.



(12) Audia, J. E.; Boisvert, L.; Patten, A. D.; Villalobos, A.; Danishefsky, S. J. *J. Org. Chem.* **1989**, *54*, 3738−3740.

(13) Zeolites having pore sizes similar to those of zeolite β (7.4 × 7.4 Å) such as zeolite Y (Y-25, 7.4 × 7.4 Å) and mordenite (M-82, 6.5 × 7.0 Å) may also be used, but zeolites with smaller pore sizes such as molecular sieves (4 Å) and zeolite ZSM-5 (5.1 × 5.4 Å) did not give any reaction. More details of the reaction conditions may be found in ref 4.

Scheme 4



To further test the scope of the BenzAll rearrangement a number of allyl benzyl ethers carrying groups other than methoxy in the para position were tested (Scheme 4). Thus, benzyloxy derivative **1n** gave aldehyde **2n** in good yield (75%). On the other hand, the TBDMS-protected derivative **1r** (Figure 1) was unreactive; the starting material was recovered in high yield. Again, steric inhibition of the delocalization of the positive charge may be the reason for the unreactivity. In this case the free electron pairs of oxygen may be prevented to participate effectively in delocalization of charge because the steric bulk of the TBDMS group forces the lone pair electrons of oxygen out of conjugation with the aromatic π-system. In addition, the lone-pair electrons may be less available for conjugation due to the neighboring silicon effect. It was shown several years ago that Lewis acids such as $SnCl_4$ did not form complexes with silyl ethers,[14,15] which recently was explained to be due to the lower coefficients of the HOMO at oxygen in silyl ethers as compared to that of corresponding alkyl ethers.[16]

Surprisingly, hydroxy compound **1s**, synthesized by deprotection of **1r** using Bu_4NF, was unreactive. A possible explanation could be protonation or Lewis acid coordination of the hydroxy group, which would counteract the charge delocalization. Both the *p*-methyl derivative **1o** and the *p*-methylthio derivative **1p** gave low yields of the corresponding 4-arylbutanals **2o** and **2p**, respectively, despite prolonged reaction times and increase of the reaction temperature to 40 °C. As expected the nitro compound **1t** failed to react. From these experiments it is obvious that to be efficient the BenzAll rearrangement needs strongly electron-donating substituents ortho or para to the benzylic carbon.

Finally, some nonbenzylic derivatives carrying groups known to be able to stabilize cations were investigated. Cyclopropyl derivative **6**[17] was not stable under the present reaction conditions (zeolite β); a multitude of products were formed as detected by TLC. The galactosyl derivative **7**,[18] on the other hand, was essentially unreactive; just a small loss of benzaldehyde was noticed. This is in contrast to the results of Ley et al.[19] who reported that simple THP-allyl ethers (the THP unit may be regarded as a simplified carbohydrate) rearranged in the presence of $SnCl_4$. However, in our case the carbohydrate carries several coordination sites for Lewis acids or protons and is also more bulky, perhaps too bulky to fit into the pores of the zeolite.

The syntheses of the allyl ether starting materials were performed by Williamson ether syntheses between the appropriate allylic halides and benzylic alcohols except for **1m**, the synthesis of which was best performed from the corresponding benzylic halide and allylic alcohol.

In conclusion, it seems necessary that strongly electron-donating substituents must be present in the aromatic ring in order to achieve high yields of the 4-arylbutanals in the BenzAll rearrangement. This requirement may be less emphasized once the conditions have been further developed. Strong activation of the aromatic ring toward electrophilic aromatic substitution leads to ring closure to give dihydronaphthalenes under the reaction conditions. In those cases where dihydronaphthalenes were not spontaneously formed, the initially formed aldehydes may be cyclized e.g. by the use of PPA as described earlier.[1,5] We also point out that the experimental procedure is very simple and should be adaptable to any scale.

Except for being aromatized to naphthalenes, dihydronaphthalenes may be used as substrates for asymmetric epoxidation,[20] dihydroxylation,[21]and Heck reactions.[22] Moreover, substituted naphthalenes and hydronaphthalenes are common features of numerous natural products and pharmaceuticals,[23−31] and much attention has been paid to improve and develop methods for their synthesis.[32] Since a vast number of allylic halides and benzylic alcohols are easily available, the BenzAll rearrangement constitutes an interesting alternative for the combinatorial synthesis of naphthalenic libraries.

Experimental Section

General. GC analyses were performed on a DBwax (J&W Scientific) capillary column 30 m × 0.25 mm i.d., 0.25 μm stationary phase. NMR spectra were recorded at 300 MHz using $CDCl_3$ as internal standard. Mass spectra were recorded in the following modes: EI (70 eV) using both direct inlet and inlet via a gas chromatograph equipped with a DB Wax column as above, CI (CH_4, 200 eV) and FAB. Chromatographic separations were performed on Matrex Amicon normal phase silica gel 60 (0.035−0.070 mm). Thin-layer chromatography were performed on Merck precoated TLC plates with Silica gel 60 F-254, 0.25 mm. After eluation, the TLC plates were visualized with UV light or sprayed with a solution of *p*-methoxybenzaldehyde (26 mL), glacial acetic acid (11 mL), concentrated sulfuric acid (35 mL), and 95% ethanol (960 mL) followed by heating. Chemicals were reagent grade. Zeolite β was a gift from EKA Chemicals AB, Bohus, Sweden, and was activated at 400 °C for 3 h before use. Zeolite β is also commercially available.[33] THF was distilled under N_2 from sodium benzophenone ketyl, and CH_2Cl_2 was distilled from P_2O_5 prior to use.

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General Procedure for the Synthesis of Allylic Ethers from Benzylic Alcohols. A solution of the appropriate benzylic alcohol (10 mmol) in THF (5 mL) was slowly added to a suspension of NaH (440 mg, 11 mmol, 60% in mineral oil) in DMF (5 mL) at 0 °C under Ar, followed by 30 min stirring. 3-Bromo-2-methylpropene or 3-bromopropene (10.3 mmol) in THF (2 mL) was then added, and the mixture was stirred for 2 h, whereafter water (1 mL) and ether (10 mL) were added. The organic phase of the resulting two-phase mixture was washed with water (5 mL) and brine (5 mL) followed by drying of the organic extract ($MgSO_4$) and concentration under reduced pressure.

3-(2-Methoxybenzyloxy)-2-methylpropene (1b). Chromatography (heptane−EtOAc, 10:1) gave 1.52 g (79%) of **1b**: ^{1}H NMR ($CDCl_3$) δ 7.43, (m, 1 H), 7.29, (m, 1 H), 6.99, (m, 1 H), 6.89, (m, 1 H), 5.06, (m, 1 H), 4.96, (m, 1 H), 4.57, (s, 2 H), 4.01, (s, 2 H), 3.85, (s, 3 H), 1.81, (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 157.1, 142.5, 128.8, 128.5, 126.9, 120.4, 112.1, 110.2, 74.4, 66.7, 55.3, 19.5. HRMS calcd for $C_{12}H_{16}O_2$ 192.1151, found 192.1151.

2-Methyl-3-(3,4-methylenedioxybenzyloxy)propene (1g). Chromatography (heptane−EtOAc, 8:2) gave 1.6 g (80%) of **1g**: ^{1}H NMR ($CDCl_3$) δ 6.87, (s, 1 H), 6.79, (m, 2 H), 5.96, (s, 2 H), 5.00, (s, 1 H), 4.94, (s, 1 H), 4.39, (s, 2 H), 3.91, (s, 2 H), 1.78, (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 147.7, 147.0, 142.2, 132.3, 121.3, 112.4, 108.5, 108.0, 101.0, 73.9, 71.7, 19.6; HRMS calcd for $C_{12}H_{14}O_3$ 206.0943, found 206.0944.

2-Methoxy-1-[((2-methylallyl)oxy)methyl]naphthalene (1k). Chromatography (heptane−EtOAc, 8:2) gave 1.81 g (71%) of **1k**: ^{1}H NMR ($CDCl_3$) δ 8.15, (d, J = 8.7 Hz, 1 H), 7.83, (m, 2 H), 7.54−7.25, (m, 3 H), 5.05, (s, 1 H), 5.02, (s, 2 H), 4.93, (s, 1 H), 4.02, (s, 2 H), 3.97, (s, 3 H), 1.78, (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 155.6, 142.7, 142.7, 133.9, 130.2, 129.2, 128.2, 126.7, 123.9, 123.6, 113.4, 112.3, 74.2, 62.0, 56.7, 19.7; HRMS calcd for $C_{16}H_{18}O_2$ 242.1306, found 242.1310.

2-Methyl-5-[((2-methylallyl)oxy)methyl]thiophene (1l). Chromatography (heptane−EtOAc, 8:2) gave 1.62 g (80%) of **1l**: ^{1}H NMR ($CDCl_3$) δ 6.79, (d, J = 3.6 Hz, 1 H), 6.61, (d, J = 3.6 Hz, 1 H), 5.01, (s, 1 H), 4.97, (s, 1 H), 4.53, (s, 2 H), 3.92, (s, 2 H), 2.48, (s, 3 H), 1.78, (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 142.0, 140.5, 138.8, 126.5, 124.6, 112.6, 73.5, 66.4, 19.6, 15.4; HRMS calcd for $C_{10}H_{15}OS$ (M + H) 183.0844, found 183.0843.

2-[((2-Methylallyl)oxy)methyl]furan (1u). Chromatography (heptane−EtOAc, 8:2) gave 0.90 g (59%) of **1u**: ^{1}H NMR ($CDCl_3$) δ 7.41, (s, 1 H), 6.34, (m, 2 H), 4.99, (s, 1 H), 4.92, (s, 1 H), 4.43, (s, 2 H), 3.93, (s, 2 H), 1.75, (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 151.9, 142.7, 141.9, 112.7, 110.1, 109.2, 73.9, 63.6, 19.5; HRMS calcd for $C_9H_{13}O_2$ (M + H) 153.0915, found 153.0922.

3-(3,4,5-Trimethoxybenzyloxy)-2-methylpropene (1m). A solution of 2-methyl-2-propenol (720 mg, 10 mmol) in THF (5 mL) was slowly added to a suspension of NaH (440 mg, 11 mmol, 60% in mineral oil) in DMF (5 mL) at 0 °C under Ar followed by 30 min of stirring. 3,4,5-Trimethoxybenzyl chloride (2.23 g, 10.3 mmol) in THF (2 mL) was then added, and the mixture was then stirred for 2 h. Workup was as described above. Chromatography of the residue (heptane−EtOAc 1:1) gave the title compound (2.17 g, 86%): ^{1}H NMR ($CDCl_3$) δ 6.57, (s, 2 H), 4.99, (m, 1 H), 4.92, (m, 1 H), 4.41, (s, 2 H), 3.92, (m, 2 H), 3.84, (s, 6 H), 3.82, (s, 3 H), 1.76, (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 153.2, 142.1, 134.1, 112.5, 105.7, 104.5, 74.1, 71.9, 60.8, 56.1, 19.6; HRMS calcd for $C_{14}H_{20}O_4$ 252.1362, found 252.1364.

3-(4-Hydroxybenzyloxy)-2-methylpropene (1s). A solution of tetrabutylammonium fluoride (TBAF) (2.5 mL, 2.5 mmol, 1 M in THF) was added dropwise to **1r** (440 mg, 1.5 mmol) in THF (30 mL) at 0 °C. The mixture was then kept at room temperature for 4 h, whereafter it was concentrated under reduced pressure. Ether (20 mL) was added to the residue, and the resulting solution was washed with aqueous saturated $NaHCO_3$ (10 mL). The organic phase was dried ($MgSO_4$) and concentrated under reduced pressure. Chromatography (heptane−EtOAc, 1:1) gave 255 mg (96%) of the title compound: ^{1}H NMR ($CDCl_3$) δ 7.28, (d, J = 8.6 Hz, 2 H), 6.89, (d, J = 8.6 Hz, 2 H), 5.08, (s, 1 H), 4.98, (s, 1 H), 4.58, (s, 2 H), 4.42, (s, 2 H), 3.92, (m 1 H), 1.80, (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 158.4, 140.8, 133.2, 128.6, 114.8, 112.7, 71.8, 67.7, 65.0, 19.4; HRMS calcd for $C_{11}H_{14}O_2$ 178.0994, found 178.0992.

General Procedure for the Rearrangement. A mixture of the appropriate allyl benzyl ether (1.0 mmol) in CH_2Cl_2 (2 mL), or the solvent indicated, and zeolite β (100 mg), activated at 400 °C for 3 h, was stirred under argon for 12 h at room temperature, unless other times and temperatures are indicated. The resulting colored mixture was then filtered through Celite, the filter cake was washed with CH_2Cl_2 (2 × 5 mL), and the combined organic extracts were concentrated under reduced pressure.

4-(2-Methoxyphenyl)butanal (2a). Chromatography (heptane−EtOAc, 95:5) gave 122 mg (69%) of **2a**: ^{1}H NMR ($CDCl_3$) δ 9.76, (t, J = 1.8 Hz, 1 H), 7.22−7.10, (m, 2 H), 6.91−6.84, (m, 2 H), 3.82, (s, 3 H), 2.68, (t, J = 7.5 Hz, 2 H), 2.44, (dt, J = 7.4 Hz, J = 1.8 Hz, 2 H), 1.94, (pent, J = 7.4 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 202.9, 157.4, 130.0, 129.6, 127.4, 120.4, 110.2, 55.2, 43.3, 29.5, 22.3; IR (film) cm^{-1} 2830, 1720; HRMS calcd for $C_{11}H_{15}O_2$ (M + H) 179.1072, found 179.1055.

1,2-Dihydro-6,7-dimethoxy-3-methylnaphthalene (2f). Chromatography (heptane−EtOAc, 10:1) gave 124 mg (61%) of **2f**: ^{1}H NMR ($CDCl_3$) δ 6.66, (s, 1 H), 6.55, (s, 1 H), 6.13, (s, 1 H), 3.87, (s, 3 H), 3.86, (s, 3 H), 2.75, (t, J = 8.2 Hz, 2 H), 2.21, (t, J = 8.3 Hz, 2 H), 1.89, (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 147.3, 147.0, 136.1, 127.9, 126.3, 122.0, 111.3, 109.1, 56.1, 28.9, 27.8, 23.4; HRMS calcd for $C_{13}H_{16}O_2$ 204.1151, found 204.1147.

1,2-Dihydro-3-methyl-6,7-methylenedioxynaphthalene (2g). Chromatography (heptane−EtOAc, 95:5) gave 118 mg (63%) of **2g**: ^{1}H NMR ($CDCl_3$) δ 6.61 (s, 1 H), 6.52, (1 s, 1 H), 6.11, (s, 1 H), 5.89, (s, 2 H), 2.72, (t, J = 8.2 Hz, 2 H), 2.19, (t, J = 8.2 Hz, 2 H), 1.89, (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 145.9, 145.3, 136.2, 129.0, 127.6, 122.4, 108.3, 106.0, 100.5, 28.9, 28.3, 23.3; HRMS calcd for $C_{12}H_{12}O_2$ 188.0837, found 188.0840.

4-(2-Methoxy-1-naphthyl)-2-methylbutanal (2k). Chromatography (heptane−EtOAc, 8:2) gave 150 mg (62%) of **2k**: ^{1}H NMR ($CDCl_3$) δ 9.71, (s, 1 H), 7.94, (d, J = 8.7 Hz, 1 H), 7.79, (m, 2 H), 7.52, (t, 1 H), 7.37, (t, 1 H), 7.29, (d, 1 H), 3.94, (s, 3 H), 3.13, (t, 2 H), 2.48, (m, 1 H), 2.06, (m,1 H), 1.70, (m, 1 H), 1.12, (d, 3 H); ^{13}C NMR ($CDCl_3$) δ 205.2, 154.3, 132.8, 129.3, 129.1, 128.6, 127.9, 126.5, 123.3, 122.9, 113.1, 56.4, 46.3, 30.7, 22.3, 13.6; IR (film) cm^{-1} 2940, 1720; HRMS calcd for $C_{16}H_{18}O_2$ 242.1306, found 242.1306.

2,5-Dimethyl-6,7-dihydrobenzo[*b*]thiophene (2l). Chromatography (heptane−EtOAc, 95:5) gave 17 mg (10%) of **2l**: ^{1}H NMR ($CDCl_3$) δ 6.43, (s, 1 H), 6.09, (s, 1 H), 2.80, (t, J = 9.0 Hz, 2 H), 2.41, (s, 3 H), 2.31, (t, J = 9.0 Hz, 2 H), 1.85, (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 142.8, 135.8, 133.5, 129.4, 123.2, 117.7, 29.8, 23.2, 23.1, 15.2; HRMS calcd for $C_{10}H_{13}S$ (M + H) 165.0738, found 165.0738.

1,2-Dihydro-5,6,7-trimethoxy-3-methylnaphthalene (2m), 1,2,3-Trimethoxy-7-methylnaphthalene (3), and 6,7,8-Trimethoxy-2-methyltetralin (4). A mixture of allyl benzyl ether **1m** (252 mg, 1.0 mmol) in toluene (2 mL) and zeolite β (100 mg) was stirred in a sealed tube at 110 °C for 18 h. The workup was as described in the general procedure for the rearrangement. Chromatography of the residue (heptane−EtOAc, 9:1) gave a 3:2:2 mixture of **2m**, **3**, and **4**, which were identified by GC−HRMS.

1,2-Dihydro-3-methyl-6,7-methylenedioxynaphthalene (2g) via BF_3·Et_2O Treatment of 5. A solution of 3,4-methylenedioxybenzyl alcohol (1.14 g, 7.50 mmol) in ether (10 mL) was added to a suspension of NaH (30 mg, 0.75 mmol, 60% in mineral oil) in ether (20 mL). The mixture was stirred for 30 min and was then cooled to 0 °C. Trichloroacetonitrile (0.75 mL, 7.5 mmol) was added, and the mixture was allowed to reach room temperature over 4 h. The solvent was evaporated under reduced pressure, and the orange residue was dissolved in heptane (15 mL) containing MeOH (32 μL) followed by filtration through Celite. Concentration of the filtrate under reduced pressure gave crude **5** as a yellow syrup, which was dissolved in cyclohexane (15 mL). To this solution was added 2-methyl-2-propenol (360 mg, 5.00 mmol) in CH_2Cl_2 (7.5 mL). After the solution was cooled to 0 °C, BF_3·Et_2O (15 μL) was added followed by 12 h of stirring at room temperature. The precipitate was then removed by filtration

through Celite, and the filtrum was washed with a 1:2 mixture of CH_2Cl_2 and cyclohexane (2 × 15 mL). The combined organic phases were washed with saturated aqueous $NaHCO_3$ (20 mL), dried ($MgSO_4$), and concentrated under reduced pressure. Chromatography of the residue (heptane−EtOAc, 8:2) gave **2g** (188 mg, 20%) and **1g** (484 mg, 47%). TLC R_f (heptane−EtOAc, 8:2) = 0.62 for **2g** and 0.23 for **1g**.

Acknowledgment. We thank the Swedish Natural Science Research Council, The Knut and Alice Wallenberg Foundation, and The Crafoord Foundation for economic support.

Supporting Information Available: ^{13}C NMR spectra for all compounds analyzed by HRMS, data for compounds **1a**, **1c**−**f**, **1h**−**j**, **1n**, **1o**−**r**, **1t**, **1v**, **2b**−**e**, **2h**−**j**, and **2n**−**p**, and stereoview of the three MM3(92)-minimized low-energy conformations of 2,3,4-trimethoxytoluene (43 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

JO980698N