Acta Chemica Scandinavica, 1998: 52: 95–99
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ACTA
CHEMICA SCANDINAVICA
ISSN 0904–213X

Mechanistic Aspects of the Zeolite β Induced Rearrangement of Alkoxybenzyl Allyl Ethers to Aldehydes and Ketones

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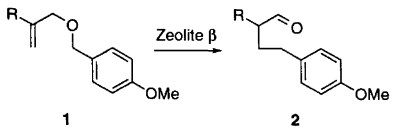
Dedicated to Professor Lennart Eberson on the occasion of his 65th birthday

Wennerberg, J. and Frejd, T., 1998. Mechanistic Aspects of the Zeolite β Induced Rearrangement of Alkoxybenzyl Allyl Ethers to Aldehydes and Ketones. – Acta Chem. Scand. 52: 95–99. © Acta Chemica Scandinavica 1998.

The mechanism for the novel zeolite β catalyzed rearrangement of alkoxybenzyl allyl ethers to aldehydes and ketones has been investigated by use of cross reactions and deuterium labeling. The reaction is mainly intramolecular and may be described as a nucleophilic attack of the double bond on the electrophilic benzylic carbon of the ether–Lewis acid complex, followed by a 1,2-hydride (or alkyl) migration.

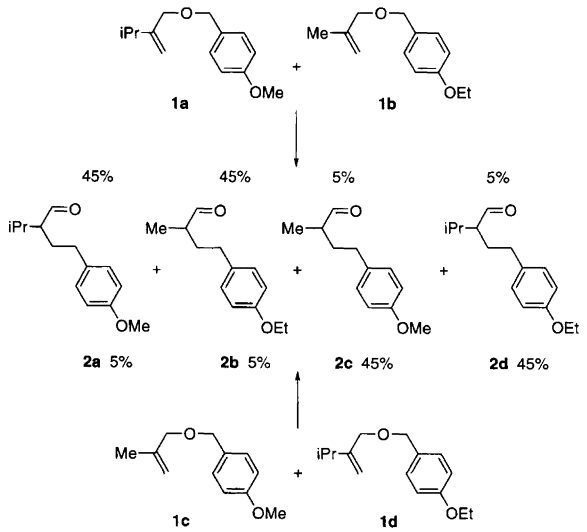
We recently found that alkoxybenzyl allyl ethers **1** rearranged under the influence of zeolite β or $BF_3 \cdot OEt_2$ to give aldehydes **2** in good yields (Scheme 1). Typical examples are *p*-methoxybenzyl (PMB) allyl ethers, although the parent benzyl allyl ether does not rearrange under these reaction conditions.[1] This, together with the fact that only zeolite β and $BF_3 \cdot OEt_2$ were effective among several Lewis acids tested, may explain why the reaction has escaped attention although benzyl allyl ethers constitute a well known class of compounds. It has been observed that bis-allylic ethers may undergo a 1,4-Wittig rearrangement to give aldehydes and/or ketones as a minor pathway under strongly basic conditions.[2]

The need for electron-donating substituents in the benzene ring indicates that a benzyl cation intermediate may be involved. In order to find out whether the mechanism is intramolecular or intermolecular cross experiments were performed. By mixing equimolar amounts of either compounds **1a**[3] and **1b** or **1c**[1] and **1d** and allowing them to rearrange under the influence of zeolite β we were able to show from the product distribution that the reaction was approximately 10% intermolecular (cross products) and 90% intramolecular (Scheme 2). The amounts of cross products could be supressed to less than 5% by diluting the reaction mixture by a factor of about 500.



1 2

Scheme 1.



Scheme 2.

By-product **3** was formed in various amounts (up to 25%) when **1a** was treated with larger portions of zeolite β. This by-product is most likely a result of a free benzyl cation attacking the aromatic ring either in the starting material or in the product.

The 1,2-hydride shift was demonstrated by using the deuteriated compound **4** as the starting material.

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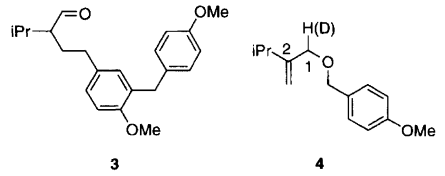
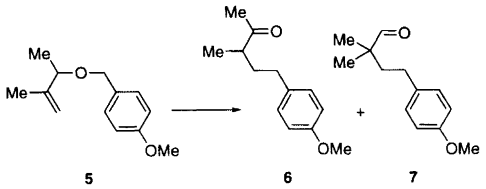


3 4

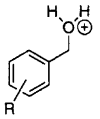
Deuterium was found to migrate from position 1 to 2 as shown by ^{1}H and ^{13}C NMR spectroscopy. Interestingly, the hydride and the deuteride migrated to the same extent according to NMR analysis (see Experimental), which was not totally unexpected since it is known that the H/D isotope effect in 1,2-migrations may be quite small.[4] Further evidence for a 1,2-bond shift was the formation of **6** and **7** (1:2) when **5** was treated with zeolite β (Scheme 3). Here competition between a hydride shift and a methyl shift occurred.



5 6 7

Scheme 3.

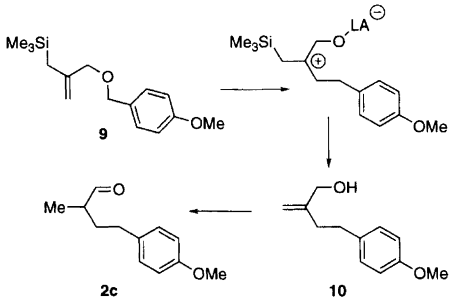
Assuming that a Lewis acid–ether complex is the first formed reactive species the C–O bond length in model oxonium ions would indicate the tendency to rearrangement. Thus, calculations (3-21 G*) of the C–O bond length of **8a** and **8b** showed that **8a** has the shorter bond length and corresponds to the benzyl allyl ether that did not rearrange. The C–O distance of **8b** is longer and so **8b** corresponds to the case that did rearrange. In several other cases there was a correlation between the tendency to rearrangement and increasing bond length, which will be reported elsewhere.[5]



8a R=H C-O = 1.6192 A
8b R=OMe C-O = 1.6367 A

For a further indication of a cationic intermediate, the rearrangement of allylsilane **9** was tested. With this substrate the intermediate tertiary carbocation was expected to undergo a β-elimination to give allylic alcohol **10**. However, aldehyde **2c**[1] was the only product isolated, probably as a result of rearrangement of **10** under the reaction conditions.[6] The alternative sequence involving a hydride migration or elimination of a proton next to the oxygen is not likely, since the putative product β-TMS aldehyde should be stable under the reaction conditions.[7] Protio-desilylation of **9** to give **1c** followed by the rearrangement would also produce **2c**. These details were not further investigated, however.

From the data presented here the following events



9 2c 10

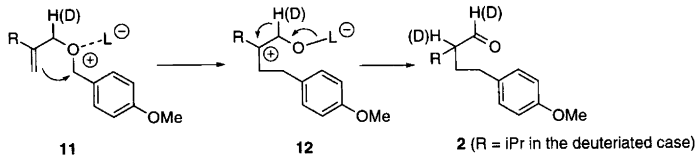
explain the results. Coordination of the Lewis acid, or possibly a proton in zeolite β, renders the benzylic carbon electrophilic and susceptible to attack by the π-electrons of the double bond (**11**). Subsequent or concomitant 1,2-bond migration followed by loss of the acid species gives the product aldehyde **2**. Although carbocation **12** was not proved to be an intermediate, such species are frequently depicted in the pinacol rearrangement and the Lewis acid induced epoxide-to-aldehyde or ketone-rearrangements.[8,9]

The alkoxybenzyl allyl ethers were synthesised by alkylation of the appropriate allylic alcoholates with different benzylic chlorides except for allylsilane **9**, which was synthesized from the corresponding allylic alcohol and 4-methoxybenzyl-2,2,2-trichloroacetimidate.[10] The deuteriated ether **4** was prepared by reduction of 2-(2-propyl)propenal[11] with sodium borodeuteride followed by alkylation of the resulting allylic alcohol with 4-methoxybenzyl chloride.

Experimental

Gas chromatographic analyses were performed on a DB Wax (J&W Scientific) capillary column 30 m, 0.25 mm i.d., 0.25 mm stationary phase. NMR spectra were recorded at 300 MHz using $CDCl_3$ as an internal standard. Chromatographic separations were performed on Matrex Amicon normal phase silica gel 60 (0.035–0.070 mm). TLC was performed on Merck precoated TLC plates (Silica gel 60 F-254, 0.25 mm). After elution the TLC plates were sprayed with a solution of *p*-methoxybenzaldehyde (2.6 ml), glacial acetic acid (1.1 ml), concentrated sulfuric acid (3.5 ml), and 95% ethanol (96 ml) and the compounds were visualized upon heating. Chemicals were reagent grade. Zeolite β was obtained from EKA Chemicals AB. THF was distilled under N_2 from sodium–benzophenone ketyl, and CH_2Cl_2 was distilled from P_2O_5 prior to use.

1-Deuterio-2-(2-propyl)-2-propenol. $NaBD_4$ (155 mg, 3.70 mmol) was added in small portions to a solution of 2-(2-propyl)propenal[11] (980 mg, 10.0 mmol) in methanol (5 ml) over 15 min at 0 °C. The mixture was stirred at room temperature for 30 min and the pH was then adjusted to 7 with 1 M HCl. Water (3 ml) was added and the resulting mixture was extracted with ether



Scheme 4. Mechanism of the rearrangement.

(3 × 5 ml), dried with $MgSO_4$ and concentrated under reduced pressure. Chromatography of the residue (heptane–EtOAc 2:1) gave 0.66 g (66%) of the title compound. ^1H NMR ($CDCl_3$): δ 5.01 (s, 1 H), 4.89 (s, 1 H), 4.11 (s, 1 H), 2.33 (m, 1 H), 1.64 (br s, 1 H), 1.08 (d, *J* 6.9 Hz, 6 H). ^{13}C NMR ($CDCl_3$): δ 155.2, 107.1, 64.6 (t, 1 C), 31.0, 21.8. IR (film) cm^{-1}: 3340br, 2950, 1460, 1045, 900. Anal. HRMS Calcd. for $C_6H_{11}DO$: 101.0951. Found 101.0952.

3-(4-Ethoxybenzyloxy)-2-methyl-1-propene (**1b**). A solution of 2-methyl-2-propenol (289 mg, 4.00 mmol) in THF (2 ml) was slowly added to a suspension of NaH (176 mg, 4.40 mmol, 60% in mineral oil) in DMF (2 ml) at 0 °C under argon, and the mixture was stirred for 30 min. 4-Ethoxybenzyl chloride (700 mg, 4.10 mmol) in THF (2 ml) was then added and the mixture was stirred for 2 h. Water (0.5 ml) and ether (5 ml) were added and the mixture was washed with water (2 ml) and brine (2 ml), after which the organic extract was dried with $MgSO_4$. The solvent was removed under reduced pressure and the residue was chromatographed (heptane–EtOAc 8:2) to give **1b** (590 mg, 72%). ^1H NMR ($CDCl_3$): δ 7.27, 6.88 (2 d, *J* 8.6 Hz, 2 H), 4.99, 4.92 (2 s, 1 H), 4.41 (s, 2 H), 4.03 (q, *J* 7.0 Hz, 2 H), 3.91 (s, 2 H), 1.77 (s, 2 H), 1.41 (t, *J* 7.0 Hz, 3 H). ^{13}C NMR ($CDCl_3$): δ 158.5, 142.3, 130.4, 129.3, 114.3, 112.3, 73.8, 71.5, 63.4, 19.6, 14.9. IR (film) cm^{-1}: 2860, 1615, 1520, 1240, 1170, 900, 820. Anal. HRMS Calcd. for $C_{13}H_{19}O_2$ (*M*+H): 207.1385 . Found 207.1382.

3-(4-Methoxybenzyloxy)-2-methyl-1-propene (**1c**) was prepared as described above from 2-methyl-2-propenol (10.0 mmol) and 4-methoxybenzyl chloride. Chromatography (heptane–ethylacetate 8:2) gave **1c** (1.87 g, 97 %). ^1H NMR ($CDCl_3$): δ 7.28, 6.88 (2 d, *J* 8.7 Hz, 2 H), 5.02, 4.94 (2 s, 1 H), 4.43 (s, 2 H), 3.92 (s, 2 H), 3.81 (s, 3 H), 1.79 (s, 3 H). ^{13}C NMR ($CDCl_3$): δ 159.1, 142.3, 130.5, 129.3, 113.8, 112.3, 73.8, 71.5, 55.3, 19.6. IR (film) cm^{-1}: 2815, 1730, 1610, 1505, 1235, 1170, 1080, 820. Anal. HRMS Calcd. for $C_{12}H_{17}O_2$ (*M*+H): 193.1228. Found 193.1227.

3-(4-Ethoxybenzyloxy)-2-(2-propyl)-1-propene (**1d**) was prepared as described above from 2-(2-propyl)-2-propenol[11] (4.00 mmol) and 4-ethoxybenzyl chloride. Chromatography (heptane–EtOAc 8:2) gave **1d** (800 mg, 85%). ^1H NMR ($CDCl_3$): δ 7.27, 6.88 (2 d, *J* 8.7 Hz, 2 H), 5.03, 4.94 (2 s, 1 H), 4.40 (s, 2 H), 4.02 (q, *J* 7.0 Hz, 2 H), 3.95 (s, 2 H), 2.37 (m, 1 H), 1.40 (t, *J* 7.0 Hz, 3 H), 1.06 (d, *J* 6.8 Hz, 6 H);^{13}C NMR ($CDCl_3$): δ 158.5, 152.1, 130.4, 129.3, 114.3, 109.4, 72.1, 71.6, 63.4, 30.9, 21.7, 14.9. IR (film) cm^{-1}: 2860, 1610, 1510, 1245, 1170, 820. Anal. HRMS Calcd. for $C_{15}H_{23}O_2$ (*M*+H): 235.1698. Found 235.1699.

4-(4-Methoxyphenyl)-2-(2-propyl)butanal (**2a**) *and 4-[3-(4-methoxybenzyl)-4-methoxyphenyl]-2-(2-propyl)-butanal* (**3**). A solution of **1a** (220 mg, 1.00 mmol) in dichloromethane (2 ml) was added to zeolite β (100 mg, activated at 400 °C for 3 h), under an argon atmosphere and then the resulting slurry was stirred for 8 h. When the reaction was complete the orange–red mixture was filtered through Celite. The Celite was washed with dichloromethane (2 × 5 ml) and the combined organic extracts were concentrated under reduced pressure. Chromatography of the residue (heptane–EtOAc 95:5) gave **2a** (166 mg, 74%) together with variable amounts of **3** (0–25%).

2a: ^1H NMR ($CDCl_3$): δ 9.68 (s, 1 H), 7.13, 6.82 (2 d, *J* 8.7 Hz, 2 H), 3.79 (s, 3 H), 2.67–2.39 (m, 2 H), 2.16–1.89 (m, 3 H), 1.78–1.65 (m, 1 H). ^{13}C NMR ($CDCl_3$): δ 205.7, 157.9, 133.7, 129.3, 113.8, 57.5, 55.3, 32.9, 28.3, 28.0, 20.2, 19.7. IR (film) cm^{-1}: 2940, 1715, 1610, 1510, 1240, 1030, 820. Anal. HRMS Calcd. for $C_{14}H_{20}O_2$: 220.1463. Found 220.1464.

(**3**) ^1H NMR ($CDCl_3$ δ 9.63 (s, 1 H) 7.14–6.75 (m, 7 H), 3.88 (s, 2 H), 3.79, 3.78 (2 s, 3 H), 2.61–2.33 (m, 2 H), 2.2–1.54 (m, 5 H), 0.96–0.91 (2 d, *J* 6.9 Hz, 3 H). ^{13}C NMR ($CDCl_3$): δ 205.8, 157.7, 155.7, 133.4, 133.2, 130.3, 129.9, 129.8, 127.0, 113.7, 110.5, 57.5, 55.5, 55.2, 35.0, 33.1, 28.3, 27.9, 20.2, 19.7. IR (film) cm^{-1}: 2920, 1715, 1500, 1240, 1160, 1030, 805. Anal. HRMS Calcd. for $C_{22}H_{28}O_3$: 340.2038. Found 340.2037.

4-(4-Ethoxyphenyl)-2-methylbutanal (**2b**). Zeolite β treatment of **1b** (1.00 mmol) as above followed by chromatography (heptane–EtOAc 95:5) gave **2b** (144 mg, 65%). ^1H NMR ($CDCl_3$): δ 9.63 (s, 1 H), 7.09, 6.82 (2 d, *J* 8.7 Hz, 2 H), 4.02 (q, *J* 7.0 Hz, 2 H), 2.66–2.56 (m, 2 H), 2.41–2.32 (m, 1 H), 2.10–1.96 (m, 1 H), 1.70–1.57 (m, 1 H), 1.41 (t, *J* 7.0 Hz, 3 H), 1.14 (d, *J* 7.0 Hz, 3 H). ^{13}C NMR ($CDCl_3$): δ 205.0, 157.3, 133.2, 129.3, 114.4, 63.4, 45.6, 32.2, 32.2, 14.9, 13.3. IR (film) cm^{-1}: 2920, 1720, 1505, 1240, 1040, 820. Anal. HRMS Calcd. for $C_{13}H_{18}O_2$: 206.1307. Found 206.1310.

4-(4-Methoxyphenyl)-2-methylbutanal (**2c**). *Route 1.* Compound **1c** (192 mg, 1.00 mmol) was treated with zeolite β as described above to give **2c** (160 mg, 83%)

after chromatography (heptane–EtOAc 95:5). ^{1}H NMR ($CDCl_3$): δ 9.63 (s, 1 H), 7.13, 6.84 (2 d, *J* 8.7 Hz, 2 H), 3.79 (s, 3 H), 2.66–2.57 (m, 2 H), 2.43–2.31 (m, 1 H), 2.30–1.97 (m,1 H), 1.70–1.57 (m, 1 H), 1.15 (d, *J* 7.0 Hz, 3 H). ^{13}C NMR ($CDCl_3$): δ 204.9, 158.0, 133.4, 129.3, 113.9, 55.3, 45.6, 32.4, 32.1, 13.4. IR (film) cm^{-1}: 2910, 1715, 1505, 1235, 1035, 820. Anal. HRMS Calcd. for $C_{12}H_{16}O_2$: 192.1151. Found 192.1146.

Route 2: via rearrangement of **9**. Compound **9** (132 mg, 0.50 mmol) was treated with zeolite β as described above to give **2c** (49 mg, 52%) after chromatography (heptane–EtOAc 8:2).

4-(4-Ethoxyphenyl)-2-(2-propyl)butanal (**2d**). Zeolite β treatment of **1d** (1.00 mmol) as described above followed by chromatography (heptane–EtOAc 95:5) gave **2d** (160 mg, 68%). ^{1}H NMR ($CDCl_3$): δ 9.64 (s, 1 H), 7.08, 6.81 (2 d, *J* 8.7 Hz, 2 H), 3.99 (q, *J* 7.0 Hz, 2 H), 2.66–2.38 (m, 2 H), 2.16–1.88 (m, 3 H), 1.78–1.65 (m, 1 H), 1.40 (t, *J* 7.0 Hz, 3 H), 0.96 (dd, *J* 4.6, 2.2 Hz, 6 H). ^{13}C NMR ($CDCl_3$): δ 205.7, 157.3, 133.6, 129.3, 114.4, 63.4, 57.5, 32.9, 28.3, 27.9, 20.2, 19.7, 14.9. IR (film) cm^{-1}: 2950, 1700, 1505, 1235, 1040, 820. Anal. HRMS Calcd. for $C_{15}H_{22}O_2$: 234.1620. Found 234.1617.

Crossover experiments. A mixture of **1a** (0,50 mmol) and **1b** (0.50 mmol) was treated with zeolite β as described. The reaction mixture was analyzed by GC (phenylcyclohexane was used as an internal standard) after 6 h, which showed the four compounds **2a–d** in the proportions presented in Scheme 2. Compounds **1c** and **1d** were treated similarly, with the result as shown in Scheme 2.

3-Deuterio-3-(4-methoxybenzyloxy)-2-(2-propyl)-1-propene (**4**) was prepared from 1-deuterio-2-(2-propyl)-2-propenol (5.00 mmol) and 4-methoxybenzyl chloride as described for **1b**. Chromatography (heptane–EtOAc 8:2) gave **4** (950 mg, 86%). ^{1}H NMR ($CDCl_3$): δ 7.26, 6.88 (2 d, *J* 8.7 Hz, 2 H), 5.06, 4.97 (2 s, 1 H), 4.43 (s, 2 H), 3.99 (s, 1 H), 3.81 (s, 3 H), 2.19 (m, 1 H), 1.05 (d, *J* 6.9 Hz, 6 H). ^{13}C NMR ($CDCl_3$): δ 159.1, 152.1, 130.6, 129.3, 113.8, 109.5, 71.7 (t, 1 C), 71.5, 55.3, 30.9, 21.7. IR (film) cm^{-1}: 2945, 1605, 1505, 1240, 1180, 815. Anal. HRMS Calcd. for $C_{14}H_{19}DO_2$: 221.1526. Found 221.1526.

Rearrangement of **4**. Compound **4** (1.00 mmol) was treated with zeolite β as above to give a mixture of 2-deuterio-4-(4-methoxyphenyl)-2-(2-propyl)butanal and 1-deuterio-4-(4-methoxyphenyl)-2-(2-propyl)butanal (155 mg, 70%) after chromatography (heptane–EtOAc 95:5). ^{1}H NMR ($CDCl_3$): δ 9.68 (s, 0.5 H), 7.11, 6.83 (2 d, *J* 8.6 Hz, 2 H), 3.79 (s, 3 H), 2.67–2.39 (m, 2 H), 2.17–1.89 (m, 2.5 H), 1.78–1.65 (m, 1 H), 0.97 (dd, *J* 4.6, 2.2 Hz, 6 H). ^{13}C NMR ($CDCl_3$): δ 205.7 (t, 1 C), 157.9, 133.7, 129.3, 113.9, 57.4 (t, 1 C), 55.3, 32.9, 28.3, 27.9, 20.2, 19.7. IR (film) cm^{-1}: 2945, 1700, 1605, 1505, 1240, 1030, 820. Anal. HRMS Calcd. for $C_{14}H_{19}DO_2$: 221.1526. Found 221.1529.

3-(4-Methoxybenzyloxy)-2,3-dimethyl-1-propene (**5**) was prepared from 3-methyl-3-buten-2-ol[12] (10.0 mmol) and 4-methoxybenzyl chloride as described for **1b**. Chromatography (heptane–EtOAc 95:5) gave **5** (1.17 g, 58%). ^{1}H NMR ($CDCl_3$): δ 7.28, 6.89 (2 d, *J* 8.7 Hz, 2 H), 4.87 (s, 2 H), 4.42 (d, *J* 11.4 Hz, 1 H), 4.21 (d, *J* 11.4 Hz, 1 H), 3.86 (q, *J* 6.5 Hz, 1 H), 3.81 (s, 1 H), 1.74 (s, 3 H), 1.28 (d, *J* 6.5 Hz, 3 H). ^{13}C NMR ($CDCl_3$): δ 159.0, 146.2, 130.9, 129.3, 113.8, 112.4, 78.4, 69.5, 55.3, 20.3, 16.9. IR (film) cm^{-1}: 1610, 1590, 1510, 1305, 1250, 820. Anal. HRMS Calcd. for $C_{13}H_{19}O_2$ (*M*+H): 207.1385. Found 207.1385.

5-(4-Methoxyphenyl)-3-methyl-2-pentanone (**6**) *and 4-(4-methoxyphenyl)-2,2-dimethylbutanal* (**7**). Compound **5** (1.00 mmol) was treated with zeolite β as described. Chromatography of the crude product (heptane–EtOAc 8:2) gave **6** (99 mg, 45%) and **7** (48 mg, 23%).

6: ^{1}H NMR ($CDCl_3$): δ 7.10 (d, *J* 8.7 Hz, 2 H), 6.84 (d, *J* 8.7 Hz, 2 H), 3.80 (s, 3 H), 2.53 (m, 3 H), 2.13 (s, 3 H), 1.99 (m, 1 H), 1.62 (m, 1 H), 1.14 (d, *J* 7.0 Hz, 3 H). ^{13}C NMR ($CDCl_3$): δ 212.6, 157.9, 133.7, 129.3, 113.8, 55.3, 46.4, 34.7, 32.5, 28.1, 16.3. IR (film) cm^{-1}: 1720, 1620, 1590, 1520, 1255, 830. Anal. HRMS Calcd. for $C_{13}H_{18}O_2$: 206.1307. Found 206.1311.

7: ^{1}H NMR ($CDCl_3$): δ 9.48 (s, 1 H), 7.09 (d, *J* 8.6 Hz, 2 H), 6.83 (d, *J* 8.6 Hz, 2 H), 3.79 (s, 3 H), 2.48 (m, 2 H), 1.76 (m, 2 H), 1.14 (s, 6 H). ^{13}C NMR ($CDCl_3$): δ 206.0, 157.9, 133.9, 129.2, 113.9, 55.3, 45.9, 39.6, 29.9, 21.4. IR (film) cm^{-1}: 2910, 1730, 1605, 1580, 1510, 1300, 1240, 820. Anal. HRMS Calcd. for $C_{13}H_{19}O_2$ (*M*+H): 207.1385. Found 207.1393.

3-(4-Methoxybenzyloxy)-2-(trimethylsilylmethyl)-1-propene (**9**). 4-Methoxybenzyl-2,2,2-trichloroacetimidate, prepared according to the literature[10] from trichloroacetonitrile (317 ml, 3.13 mmol) and 4-methoxybenzyl alcohol (433 mg, 3.13 mmol), was dissolved in cyclohexane (5 ml). A solution of 2-[(trimethylsilyl)methyl]-2-propen-1-ol (purchased from Aldrich, 288 mg, 2.00 mmol) in dichloromethane (2.5 ml) was then added. The resulting solution was cooled to 0 °C and treated with $BF_3 \cdot OEt_2$ (5 μL). The reaction mixture was warmed to room temperature and stirred overnight. The white precipitate was then removed by filtration through Celite and the residue was washed with a 1:2 mixture of dichloromethane and cyclohexane (2 × 5 ml). The filtrate was washed with saturated aqueous $NaHCO_3$ (5 ml), dried over $MgSO_4$ and concentrated under reduced pressure. Chromatography of the residue (heptane–EtOAc 8:2) gave **9** (295 mg, 56%). ^{1}H NMR ($CDCl_3$): δ 7.28 (d, *J* 8.7 Hz, 2 H), 6.88 (d, *J* 8.7 Hz, 2 H), 4.42 (s, 2 H), 3.84 (s, 2 H), 3.78 (s, 3 H), 0.15 (s, 2 H), 0.03 (s, 9 H). ^{13}C NMR ($CDCl_3$): δ 159.1, 143.9,

129.3, 129.2, 113.7. 109.2, 73.9, 71.5, 55.3, −0.4, −1.4. IR (film) cm^{-1}: 2950, 1610, 1510, 840. Anal. HRMS Calcd. for $C_{15}H_{24}O_2Si$: 264.1545. Found 264.1546.

Acknowledgements. We thank the Swedish Natural Research Council, the Knut and Alice Wallenberg Foundation and the Crafoord Foundation for financial support.

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Received April 1, 1997.