Cyclialkylation of Arylalkyl Epoxides with Solid Acid Catalysts

Jacob A. Elings,[a][+] Roger S. Downing,[a] and Roger A. Sheldon*[a]

Keywords: Friedel-Crafts reaction / Hydroxyalkylation / Aromatics / Epoxides / Zeolites / Clays

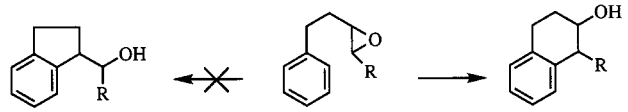
Solid acids, such as zeolites and clays, catalyse the intramolecular hydroxyalkylation (cyclialkylation) of several arylalkyl epoxides in moderate to excellent conversions and selectivities. The use of solid acids in these cyclialkylations provides a cleaner, better alternative to conventional Lewis and Brønsted acids, enabling a more facile workup of reaction mixtures and, in several cases, better selectivities.

Introduction

As part of an ongoing study on the use of solid acid catalysts in organic synthesis,[1] we are interested in the hydroxyalkylation of aromatics with epoxides. The hydroxyalkylation of benzene with ethylene oxide and 1,1,2,3,3-pentamethylindane with propylene oxide, for example, are employed industrially for the synthesis of important fragrance chemicals.[2][3] Our previous attempts to catalyse the hydroxyalkylation of benzene with propylene oxide, which was chosen as a model reaction, using solid acids afforded only very poor yields (< 2%). We attributed this to an "adsorption imbalance", i.e. the more polar epoxide is preferentially adsorbed on the catalyst leading to extensive epoxide polymerisation at the expense of the desired hydroxyalkylation.[4][5] In order to demonstrate that solid-acid-catalysed hydroxyalkylation is in principle possible, we circumvented the above problem by combining the aromatic ring and the epoxide moiety in the same molecule. Hence, we now report on the successful intramolecular hydroxyalkylation (cyclialkylation) of arylalkyl epoxides over solid acid catalysts.

The Friedel-Crafts cyclialkylation of arylalkyl epoxides mediated by conventional Lewis and Brønsted acids (e.g., $SnCl_4$, $BF_3{\cdot}Et_2O$ and CF_3CO_2H) has been extensively investigated by Taylor and co-workers.[6–9] Cyclialkylation led to the exclusive formation of six-membered rings (Scheme 1). The cyclialkylation of arylalkyl epoxides belongs to the family of reactions in which the epoxide function has been employed as the trigger for cationic cyclisations. In this way, various organic molecules, many of which with biological interest, have been prepared from epoxy-olefin[10][11] and epoxy-arene[12–17] compounds.

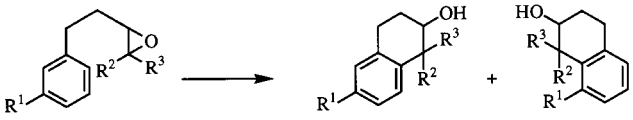
Since the classical cyclialkylation generally involved the use of stoichiometric amounts of Lewis and Brønsted acids, a method employing catalytic amounts of a recyclable solid acid catalyst would constitute a substantial improvement on the existing methodology.[18]



Scheme 1.Cyclialkylation of an arylalkyl epoxide

Results and Discussion

We have studied the cyclialkylation of arylalkyl epoxides employing various zeolites in their protic forms and a commercial acidic montmorillonite clay. The substrates investigated were 4-phenyl-1-butene oxide (**1a**), its *m*-methoxy derivative (**1c**) and congeners of these with single and double methyl substitution at the terminal epoxide carbon atom (**1b**, **1d** and **1e**). Scheme 2 shows these substrates and their expected tetrahydronaphthol products.



	R^1	R^2	R^3		
1a	H	H	H	**2a**	
1b	H	Me	Me	**2b**	
1c	OMe	H	H	**2c**	**3c**
1d	OMe	H	Me	**2d**	**3d**
1e	OMe	Me	Me	**2e**	**3e**

Scheme 2. Substates and expected cyclialkylation products in the solid-acid-catalysed cyclialkylation of arylalkyl epoxides

Catalyst Comparison

Treatment of parent compound **1a** with the various heterogeneous catalysts in refluxing benzene gave 1,2,3,4-tetrahydro-2-naphthol (**2a**) as the only cyclialkylation product.

[a] Laboratory of Organic Chemistry and Catalysis, Delft University of Technology,
Julianalaan 136, NL-2628 BL Delft, The Netherlands
Fax: (internat.) + 31(0)15/2781415
E-mail: R.A.Sheldon@stm.tudelft.nl
[+] Present address: Department of Chemistry, The University of York,
Heslington, York YO10 5DD, United Kingdom

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Table 1. Solid-acid-catalysed cyclialkylation of 4-phenyl-1-butene oxide (**1a**) to 1,2,3,4-tetrahydro-2-naphthol (**2a**) in refluxing benzene[a]

Entry	Catalyst	mmol **1a**/g catalyst	Time [min]	Conv. (%)	mmol **1a** conv./g catalyst	Sel. **2a** (%)
1	H-mordenite	3.52	120	57.2	2.01	37.4
2	H-mordenite	3.52	1200	86.9	3.06	31.9
3	H-mordenite	7.17	120	26.5	1.90	30.3
4	H-mordenite	7.17	1200	51.5	3.69	24.0
5	H-mordenite	13.8	120	12.7	1.75	24.8
6	H-mordenite	13.8	1200	26.2	3.61	18.9
7	H-beta	3.68	15	100	3.68	20.4
8	H-beta	3.68	120	100	3.68	6.5
9	H-beta	3.68	1200	100	3.68	0.0
10	H-beta	13.8	120	45.3	6.25	23.7
11	H-beta	13.8	1200	49.8	6.87	22.2
12	Mont. K10	3.80	120	100	3.80	7.2
13	Mont. K10	3.80	1200	100	3.80	5.1
14	Mont. K10	14.2	120	100	14.2	4.0
15	Mont. K10	14.2	1200	100	14.2	2.3
16	Nafion NR50	6.08[b]	120	53.3	3.24	1.2
17	Nafion NR50	6.08[b]	1200	100	6.08	0.0

[a] Conditions: epoxide **1a**; internal standard 1,3,5-tri-*tert*-butylbenzene (1 mmol); benzene (100 ml); catalyst (0.5 g); reflux conditions (80°C). – [b] Amount of catalyst (0.3 g).

This product is as expected from hydroxyalkylation by epoxide and not by aldehyde or ketone products of a possible epoxide rearrangement. It is noteworthy that, despite numerous attempts, the cyclisation of **1a** has never been achieved under homogeneous Lewis or Brønsted acid conditions.[6] Table 1 shows that the acidic forms of the zeolites and montmorillonite K10 were able to bring about the conversion of **1a** into **2a** in low to moderate selectivities. Acid resin Nafion NR50 gave only a trace of **2a** (entry 16). H-beta (entry 7) and montmorillonite K10 already showed complete conversions after only 15 min at the lowest epoxide concentration. Although H-beta gave initially a moderate selectivity to **2a** (entry 7), this product was rapidly decomposed (see later) upon prolongation of refluxing (entry 8 and 9). Despite its high activity, the clay catalyst gave only a low selectivity to **2a** (entries 12–15). The best results were obtained with H-mordenite as the catalyst. However, comparison of the conversions of **1a** at 2 h (entries 1, 3 and 5) and 20 h (entries 2, 4 and 6) shows that this zeolite was prone to deactivation. In contrast, the activity of H-beta and montmorillonite K10 appeared both to be much higher and to be maintained for longer, which might be explained by their higher acidity, more open structure and higher outer-surface activity.

The major by-products which could be detected by GC and GC/MS were dehydration products, rearrangement products such as aldehyde, and higher boiling compounds from epoxide **1a** and/or its derivatives resulting from their polymerisation and condensation with benzene. The decomposition of **2a** observed upon prolonged heating under reflux is presumably partially due to its dehydration. Probably, deposition of insoluble polymerisation and condensation products on the surface of H-mordenite was responsible for the observed catalyst deactivation.

It was expected that when the cyclialkylations were performed in more dilute suspensions, side reactions such as epoxide polymerisation could be suppressed. Indeed, lowering of the initial amount of epoxide **1a** in the H-mordenite-catalysed cyclialkylation had a significant beneficial effect on the selectivity to **2a**, which is in particular illustrated by entries 1 and 4 at approximately the same conversion values. Paradoxically, a substantial increase of the epoxide concentration in the H-beta-catalysed cyclialkylation resulted in a higher selectivity to **2a** (entry 10). However, comparison of the conversions at 120 min (entry 10) and 1200 min (entry 11) showed that H-beta at this higher concentration was strongly deactivated and was therefore no longer able to catalyse consecutive reactions such as dehydration. The results with H-mordenite and H-beta also suggest that the cyclialkylation is more favourable in the initial stage of the reaction and that undesired reactions such as polymerisation predominate in a later stage of the reaction. Apparently, the formation of cyclialkylation product **2a** causes its own downfall, suggesting that it is involved in polymerisation.

Substituent Effects

Studies with conventional acids have previously shown that (six-membered) cyclialkylation of arylalkyl epoxides at primary epoxide positions is not facile.[6] Substitution of the epoxide ring by electron-releasing substituents may increase its reactivity when the cyclialkylation proceeds by a borderline S_N2 mechanism, because in this way a developing positive charge during the epoxide ring opening will be better accommodated. Indeed, constructing a tertiary epoxide carbon atom at the alkyl terminus of **1a** to form 2-methyl-5-phenyl-2-pentene oxide (**1b**) resulted in a much higher reactivity of the epoxide. In this case, a switch from an S_N2 to an S_N1 mechanism may even occur because a carbenium ion can be easily stabilised by the presence of the electron-releasing methyl groups. Furthermore, the presence of these groups will sterically disfavour an S_N2 attack. Treatment of epoxide **1b** with H-mordenite and H-beta in benzene resulted in a rapid conversion of this com-

pound, even at room temperature, leading to the formation of the expected cyclialkylation product (**2b**). Furthermore, a variety of rearrangement products such as ketones and allylic alcohols (**4**−**7**) were formed (see Figure 1).

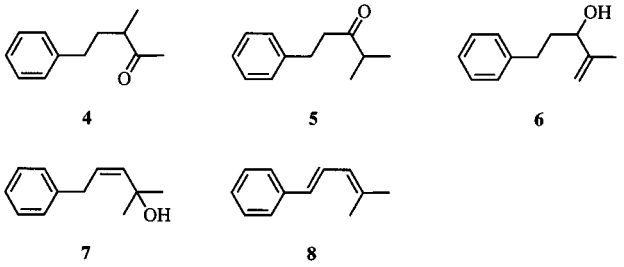


Figure 1. Major by-products formed during the cyclialkylation of epoxide **1b**

Most of these reaction products were prone to dehydration, especially under reflux conditions. Various dehydration products were detected by GC/MS. Remarkably, nearly identical fragmentation patterns were observed for the different dehydration products, suggesting the formation of a common intermediate after the electron impact. Prolonged refluxing resulted in disappearance and appearance of different dehydration products, leading, finally, to the predominant occurrence of one of them; presumably the energetically favourable conjugated phenylbutadiene **8**.

Table 2 shows that catalytic amounts of H-mordenite and H-beta were able to convert **1b** rapidly into products **2b** and **4**−**7** with high total selectivities (ranging from 93 to 96%) at room temperature, affording cyclialkylation product **2b** in moderate selectivities (26−36%). Turnover numbers, defined as the molar ratio between consumed epoxide and bulk aluminium, up to 23 were obtained. Although H-beta gave a very rapid conversion of **1b** into **2b** in refluxing benzene, initially with a moderate selectivity, the cyclialkylation product was prone to dehydration under these conditions. Treatment of **1b** with conventional Lewis acids afforded cyclialkylation product **2b** in low to moderate yields.[8] In the latter case, the best yield (24%, determined by internal-standard GC analysis) was obtained by using 0.1 equiv $BF_3{\cdot}Et_2O$ in dichloromethane at room temperature. It is clear, therefore, that our solid-acid-catalysed approach provides a useful, truly catalytic, alternative to this classical homogeneous system.

In contrast to epoxide **1a**, treatment of **1b** with solid acids did not result in the formation of significant amounts of higher boiling compounds and catalyst deactivation. Presumably, the presence of the two terminal methyl groups in the epoxide forms a steric hindrance to polymerisation. However, steric hindrance may also inhibit cyclialkylation which may explain the strong tendency of **1b** to rearrange to ketones and aldehydes, which only require shifts of relatively small groups (hydride and methyl).

Intramolecular hydroxyalkylation of 4-(3-methoxyphenyl)-1-butene oxide (**1c**) may result in both *ortho*-alkylation and *para*-alkylation (see Scheme 2). Indeed, Taylor and coworkers found that reaction of **1c** with 2 equiv of $SnCl_4$ in refluxing dichloromethane for 4 h afforded a mixture of 6-methoxy-1,2,3,4-tetrahydro-2-naphthol (**2c**) and 8-methoxy-1,2,3,4-tetrahydro-2-naphthol (**3c**) in a combined yield of 30−34% and a ratio of 2.8.[6] Table 3 shows that the treatment of epoxide **1c** in refluxing benzene and chlorobenzene with various solid (Brønsted) acids also resulted in the formation of tetrahydronaphthols **2c** and **3c**. For example, H-mordenite, H-beta and montmorillonite K10 were able to catalyse the cyclialkylation of **1c** to **2c** and **3c** in moderate yields (26−40%) and mass balances.

Table 3. Cyclialkylation of 4-(3-methoxyphenyl)-1-butene oxide (**1c**) with various solid acids[a]

Catalyst	Time [min]	Conv. (%)	Selectivity **2c** + **3c** (%)	Ratio **2c**/**3c**
NaHY	60	11.3	24.7	2.4
NaHY	1380	22.3	25.1	2.5
H-mordenite	60	53.4	62.2	3.2
H-mordenite	210	60.1	60.3	3.1
H-mordenite[b]	60	84.2	47.1	2.0
H-beta	60	100	33.4	2.1
H-beta	210	100	25.5	1.6
Mont. K10	60	100	27.7	1.6

[a] Conditions: epoxide **1c** (2.8 mmol); internal standard 1,3,5-tri-*tert*-butylbenzene (1 mmol); benzene (100 ml); catalyst (0.5 g); reflux conditions (80°C). − [b] Performed in chlorobenzene at 132°C.

GC/MS revealed also, but to a lesser degree, the presence of dehydration and rearrangement products (e.g., aldehyde) in the reaction mixture. A large amount of higher boiling compounds was observed, which could explain a significant part of the missing mass balance. Coke formation from the starting material and/or reaction products, suggested by the strong discolouration of the catalysts, may also partially explain loss of material and the rapid decrease of the activity of H-mordenite. The results with H-beta show that the

Table 2. Solid-acid-catalysed rearrangement of 2-methyl-5-phenyl-2-pentene oxide (**1b**) in benzene[a]

Catalyst	Temp [°C]	Time [min]	Conv. (%)	Selectivity (%)					
				2b	**4**[b]	**5**	**6**	**7**	**8**
H-mordenite	r.t.	15	21.5	35.8	9.8	17.2	8.4	21.5	0.0
H-mordenite	r.t.	480	83.4	26.4	12.1	20.4	13.4	23.5	0.0
H-beta	r.t.	15	76.5	26.7	10.6	14.6	14.5	26.1	0.0
H-beta	r.t.	480	100	26.6	10.9	16.8	16.3	22.6	0.0
H-beta	80	5	100	23.2	15.8	26.2	14.7	8.6	0.0
H-beta	80	1440	100	0.0	2.6	39.7	0.0	0.0	33.2

[a] Conditions: epoxide **1b** (6.5 mmol); internal standard 1,3,5-tri-*tert*-butylbenzene (1 mmol); benzene (100 ml); catalyst (0.25 g). − [b] GC/MS data were consistent with structure **4** in Figure 1 (see Experimental Section).

tetrahydronaphthols in this case are also prone to decomposition upon prolonged heating under reflux. Nevertheless, the solid acid approach of cyclialkylation of **1c** is interesting because the turnover numbers, defined as the molar ratio between consumed epoxide and tin or bulk aluminium are higher (up to 6), the reaction conditions milder, the reaction times shorter and the yields comparable to or even somewhat better than in the classical system. Furthermore, the products are easier to isolate without the need of neutralisation steps during the workup, simply by filtering or centrifugation of the reaction mixture and distilling the solvent. Moreover, the purification is improved because the formation of undesirable by-products,[6] such as diols (due to attack of water on unreacted epoxide during acidic workup) and chlorohydrins, can be reduced or prevented.

In general, conventional Lewis acids in Friedel-Crafts reactions may form strong complexes with both the reactant and product thus necessitating the use of stoichiometric amounts of these catalysts. Moreover, these complexes have to be decomposed by aqueous acidic workup and, as a result, the catalyst is usually not recovered. It should be noted, however, that the choice of 2 equiv. $SnCl_4$ in the cyclialkylation of **1c** by Taylor and co-workers was mainly based on a general procedure designed to ensure that reactions of a wide variety of epoxides would proceed to completion. The same investigators showed for some other substrates that catalytic quantities of a Lewis acid can be sufficient to transform these types of epoxide in good yields to the cyclialkylation products.[7][8]

Comparison of the results in Table 3 with those in Table 1 shows that the cyclialkylation of **1c** afforded higher selectivities to the tetrahydronaphthols than that of **1a**. This can be explained by two effects of the methoxy group in **1c**. First, the activating methoxy group will promote, due to its electron-releasing mesomeric effect, the nucleophilicity of the *ortho*- and *para*-positions (with respect to this group) of the aromatic ring and therefore the susceptibility to ring closure. Second, the sensitivity of the tetrahydronaphthols to decomposition (e.g., dehydration) appeared to be decreased in the presence of the methoxy group. The latter effect is in particular illustrated by the results with H-beta and H-montmorillonite. A possible explanation may be that coordination of the methoxy oxygen atom with acid sites results in a decrease of the effective acidity of the solid catalysts. Moreover, the higher electron density of the aromatic ring, due to the presence of the methoxy group, probably makes proton elimination from the neighbouring 1-position of the tetrahydronaphthols, and therefore dehydration, more difficult.

Constructing a secondary epoxide carbon atom at the terminus of **1c** to form 5-(3-methoxyphenyl)-2-pentene oxide (**1d**) was expected to promote cyclialkylation. Indeed, Table 4 shows that treatment of epoxide **1d** with H-mordenite resulted in a rapid and very selective conversion of this epoxide into the expected tetrahydronaphthols **2d** and **3d**. Although in this case larger amounts of epoxide were used than in the reaction of **1c** with H-mordenite (see Table 3), an almost complete conversion was obtained (turnover numbers up to 10) and no deactivation of the catalyst was observed. For this study, a mixture of *trans*/*cis* isomers of **1d** was used (*trans*/*cis* = 3.89) and the corresponding isomers of tetrahydronaphthols **2d** and **3d** were obtained in roughly the same ratio as that of epoxide **1d** indicating that the cyclialkylation of **1d** proceeded with a high degree of stereospecificity. The small deviation of the ratios found for **2d** may be explained by a difference in sensitivity to consecutive reactions of this tetrahydronaphthol. A very high degree of stereospecificity (97%) was also observed in the cyclialkylation of a *trans*/*cis* mixture of 5-phenyl-2-pentene oxide with $SnCl_4$ in refluxing dichloromethane.[7] Our results indicate that this stereospecificity is not influenced by the presence of a methoxy group or by the use of a solid acid instead of a homogeneous Lewis acid.

As mentioned above, the cyclialkylation of **1b** was accompanied by the formation of large amounts of rearrangement products. Pocker and Ronald stated that epoxide rearrangements in the presence of acids can, generally, be made to dominate by using weakly nucleophilic media.[19] Conversely, an increase of the nucleophilicity of the medium should result in a decreased tendency to rearrange. The reaction of 5-(3-methoxyphenyl)-2-methyl-2-pentene oxide (**1e**) with H-mordenite to its corresponding tetrahydronaphthols (**2e** and **3e**) shows that this principle is also applicable to intramolecular systems. Table 5 shows that the increase of the nucleophilicity of the aromatic group of **1b** by the introduction of a *meta*-methoxy group resulted in a drastic increase in the selectivity to the cyclialkylation products and disfavoured the formation of rearrangement products (**9** and **10**, see Figure 2). Remarkably, longer periods at reflux did not affect the selectivities to the cyclialkylation products. The high stability of tetrahydronaphthols **2e** and **3e** can be attributed to the absence of easily abstractable benzylic protons at the 1-position.

Mechanistic Aspects

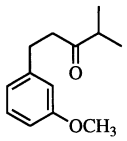
Concerning the reaction mechanism, two modes of cyclisation were proposed for arylalkyl epoxides;[7] direct attack of the epoxide carbon atom at the position *ortho* to the alkyl chain giving a six-membered ring intermediate and, alternatively, attack at the *ipso*-position giving a five-membered ring spiro intermediate that subsequently rearranges to a six-membered ring intermediate. Because the latter cyclisation mode would give rise to two different rearrangement products with unsymmetrical arylalkyl epoxides and the fact that just one of these products, identical to that expected from a direct attack, is predominantly formed, we conclude that cyclisation via a spiro intermediate does not occur to any appreciable extent.

The requirement of Brønsted and Lewis acids in the cyclialkylation of arylalkyl epoxides suggests that bond weakening of the epoxide to a cation-like species precedes the actual bond making, indicating that the epoxide carbon atoms carry at least a fractional positive charge.[6][20] Although electron-releasing substituents have a beneficial effect on

Table 4. Cyclialkylation of a *trans*/*cis* mixture of 5-(3-methoxyphenyl)-2-pentene oxide (**1d**) with H-mordenite in refluxing benzene[a]

mmol **1d**/g catalyst	Time [min]	Conv. (%)	Selectivity **2d** + **3d** (%)	Ratio **2d**/**3d**	*trans*/*cis* **2d**	*trans*/*cis* **3d**
10.1	120	98.9	93.5	2.2	3.4	3.9
18.2	1200	97.5	91.8	2.2	3.3	3.8

[a] Conditions: epoxide **1d** (*trans*/*cis* = 3.89); internal standard 1,3,5-tri-*tert*-butylbenzene (1 mmol); benzene (100 ml); catalyst (0.5 g); reflux conditions (80°C).



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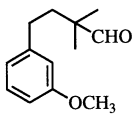

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Figure 2. Byproducts formed in the cyclialkylation of **1e**

Table 5. Cyclialkylation of 5-(3-methoxyphenyl)-2-methyl-2-pentene oxide (**1e**) with H-mordenite in refluxing benzene[a]

Time [min]	Conv. (%)	Selectivity (%) **2e** + **3e**	Selectivity (%) **9** + **10**[b]	Ratio **2e**/**3e**
15	100	67.6	18.5	2.0
120	100	67.6	19.7	2.0

[a] Conditions: epoxide **1e** (5.3 mmol); internal standard 1,3,5-tri-*tert*-butylbenzene (1 mmol); benzene (100 ml); H-mordenite (0.5 g); reflux conditions (80°C). — [b] Products **9** + **10** could not be separated by GC analysis.

the cyclialkylation, due to their stabilising effect on a positive charge, an S_N1 mechanism is precluded in most cases. An S_N1 mechanism is not consistent with the observed attack at primary positions, since the formation of primary carbocations is unlikely. Furthermore, the observed stereospecificities for the molecules mentioned in the previous section can only be explained by an S_N2-type mechanism in which inversion of configuration takes place. This indicates that the carbenium ion character of the epoxide moiety of an arylalkyl epoxide should be low in the cyclialkylation process, or that its truly cationic character is reduced by the formation of a partial bond to the epoxide oxygen. Both suggestions are consistent with a borderline S_N2 mechanism.[20]

Although epoxides can open in either of two directions, only six-membered rings were formed (see Scheme 1) consistent with previous studies of homogeneous arylalkyl epoxide cyclialkylations.[6–9] No five-membered ring isomer was observed, even when this would involve nucleophilic attack at the more substituted carbon atom, which is more able to accommodate a positive charge (e.g., in the cyclialkylation of **1a** and **1c**). The failure to form five-membered rings was also observed when epoxides were used with primary or secondary positions which were only capable of undergoing five-membered cyclialkylation.[6] This behaviour indicates conclusively that steric constraints may dominate the cyclisation reaction and can be reasonably explained by a difficult attainment of collinearity of the nucleophilic carbon atom and departing epoxide oxygen atom upon formation of five-membered rings.[21]

Catalyst Regenerability

Since the use of solid acids is particularly of interest when these can be regenerated, the reusability of H-mordenite was investigated. Table 6 shows that regeneration of H-mordenite did not result in loss of activity or selectivity and even led to a small but significant increase of the selectivity to **2a**. An explanation for this improvement might be that the regeneration process, in particular the thermal reactivation, created a more open structure of H-mordenite, enabling more space for epoxide **1a** to achieve an optimum conformation for the cyclialkylation. The regenerability results indicate that substantial coke formation may cause the deactivation of H-mordenite. Indeed, thermogravimetric analysis (TGA) of spent H-mordenite revealed that after the reaction a relatively large amount of organic material was present on the solid catalyst, resulting in a substantial increase of the catalyst weight (see Figure 3). Assuming that the organic material mainly consists of polymers of epoxide **1a** and that at 400–500°C this material was totally removed, regenerating the original solid, it can be estimated that 8 weight per cent of the starting amount of this epoxide was deposited on the catalyst. The TGA plot also shows that heating of the spent catalyst in air to approximately 450°C is sufficient to remove this deposit totally; a fact which is supported by the results from Table 6 and the white colour of the recovered catalyst. TGA also shows that a reactivation at a temperature higher than 500°C would result in a deleterious decomposition of H-mordenite.

Table 6. Catalyst regenerability in the cyclialkylation of 4-phenyl-1-butene oxide (**1a**) with H-mordenite in refluxing benzene[a]

Cycle	Conv. (%)	Selectivity **2a** (%)
0	45.8	22.0
1	50.2	27.3
2	47.1	30.7

[a] Conditions (cycle 0): epoxide **1a** (10.5 mmol); internal standard 1,3,5-tri-*tert*-butylbenzene (3 mmol); benzene (300 ml); H-mordenite (1.5 g); reflux conditions (80°C); reaction time (20 h). After this, the catalyst was removed by centrifugation, washed with benzene (2 × 100 ml), dried at 120°C for 24 h and subsequently reactivated at 450°C. In each cycle the amounts of epoxide, internal standard and solvent were adapted to the amount of catalyst which remained after its recovery and reactivation.

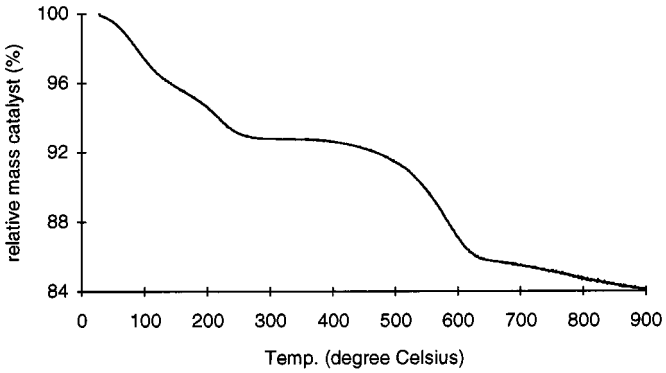

Figure 3. TGA plot of H-mordenite (from cycle 0 of Table 6) after use in the cyclialkylation of epoxide **1a**, heated in a stream of air

Conclusions

Intramolecular experiments using epoxides incorporated in aromatic molecules show that solid (Brønsted) acid catalysed hydroxyalkylation of aromatics is in principle possible and that truly catalytic reactions can be achieved. In contrast to the intermolecular counterparts of these reactions, solid acids proved to be effective catalysts in intramolecular cyclisations, giving moderate to excellent conversions and selectivities to the hydroxyalkylation products. This is illustrated by an intermolecular counterpart of the effective and selective hydroxyalkylation of **1d**, the reaction between anisole and propylene oxide, which gave only oligomers of the epoxide in 51% yield.[4][5]

Comparison of the heterogeneous results with examples from the literature in which conventional acids were used, showed that the use of solid acids in these cyclialkylations provides a cleaner, better alternative to conventional acids, which also enables a more facile workup of reaction mixtures. For some arylalkyl epoxides, the use of solid acids in cyclialkylations may prove to be of considerable synthetic potential.

Experimental Section

General: All chemicals used were analytical grade products purchased from commercial suppliers and were used without further purification. All glassware was dried at 140°C for at least 1 h prior to use in the catalytic reactions. − Gas chromatography (GC) analyses were performed with a Varian Star 3600 gas chromatograph equipped with a flame-ionisation detector and a Chrompack CP Sil 5 CB wide-bore column (50 m × 0.53 mm) using nitrogen as a carrier gas. − Gas chromatography/mass spectrometry (GC/MS) analyses were performed with a VG 70-SE mass spectrometer equipped with a CP Sil 5 CB column. The mass spectra were obtained in the electron impact (EI) mode using 70 eV as ionisation energy. − ^{1}H-NMR spectra of solutions in $CDCl_3$ were recorded with a Varian T-60 spectrometer (at 60 MHz), an INOVA-300 spectrometer (at 300 MHz) or a Varian VXR-400S spectrometer (at 400 MHz). − ^{13}C-NMR spectra of solutions in $CDCl_3$ were recorded with an INOVA-300 spectrometer (at 75 MHz) or a Varian VXR-400S spectrometer (at 100 MHz). The chemical shifts δ are reported in parts per million (ppm) downfield from tetramethylsilane (TMS). ^{13}C-NMR signals were assigned by the attached proton test method (APT) and correlation tables. − Column chromatography was performed with silica gel 60 (particle size 0.063−0.200 mm) from Merck. The fractions were investigated by TLC and GC. − Thin layer chromatography (TLC) was performed on pre-coated silica gel plates (Merck silica gel $60F_{254}$). The plates were first observed under UV light (254 nm) and then after staining with a 2.5 wt-% aqueous $KMnO_4/K_2CO_3$ solution followed by warming with a blow-drier. − The solid catalysts were characterised by X-ray powder diffraction (XRD) using a Philips PW 1877 diffractometer with Cu-K_α radiation. − Thermogravimetric analyses (TGA) of spent catalysts were carried out with an STA-1500 H thermobalance (PL Thermal Sciences). TGA was performed by heating 10 mg of the spent catalyst at a rate of 10°C/min in an air flow of ca. 50 ml/min. − The silicon, aluminium and sodium contents of the solid catalysts were determined by elemental analysis with inductive coupled plasma atomic emission spectroscopy (ICP-AES) and atomic absorption spectroscopy (AAS). The samples of the solid catalysts were prepared by successive addition, to 30 mg of catalyst which was weighed into a plastic bottle, of 45 ml water, 2.25 ml 20 wt-% aqueous sulfuric acid and 0.45 ml 40 wt-% aqueous hydrofluoric acid. The bottle was subsequently shaken at room temp. overnight. The measurements were recorded with a Perkin−Elmer Plasma 40 (ICP-AES) or a Perkin−Elmer 1100 (AAS) instrument.

Origin of the Catalysts: Mordenite (sodium form, Si/Al = 7.3, Al/Na = 1.0) was obtained from PQ zeolites. The ammonium form of mordenite (batch A: Si/Al = 6.7, Al/Na = 17 and batch B: Si/Al = 7.7, Al/Na = 16) was obtained by ion exchange with 1 M aqueous ammonium nitrate at 80°C for 24 h. Batch A was used in the experiments with 2-methyl-5-phenyl-2-pentene oxide (**1b**). Batch B was used in the experiments with all other epoxides. − Zeolite beta (Si/Al = 12, Al/Na = 10) was synthesised according to a modified method of Wadlinger et al.[22] A polypropylene bottle equipped with a magnetic stirrer bar was charged with sodium aluminate (8.71 g, Riedel-de Haën, 54% Al_2O_3, 92.3 mmol Al), 40 wt-% aqueous tetraethylammonium hydroxide (82.52 g, 224 mmol) and water (5 ml). After closing of the bottle, the mixture was stirred in a boiling water bath for 1 h. The resulting clear solution was transferred to a Teflon insert, which was, prior to its use, successively cleaned with diluted aqueous hydrogen fluoride (at room temp.), 2 M aqueous sodium hydroxide (at 80°C) and copious water. To this solution was slowly added silica sol (218.72 g, Ludox LS, 30 wt-%, 1092 mmol) under mechanical stirring. After stirring of the immediately formed thick smooth gel at room temp. for one night, the Teflon insert was placed into an autoclave and heated at 150°C for 166 h. A crystalline material was obtained, which was centrifuged, thoroughly washed with water until the supernatant liquid was pH-neutral and dried over potassium hydroxide under vacuum. This resulted in 89 g as-synthesised beta in the form of a fine white powder. To obtain a complete removal of the template, the as-synthesised zeolite was subjected to three subsequent calcination steps. First, it was calcined in air to 450°C for 23 h (heating rate 1°C/min). After cooling to room temp., this was followed by a second calcination in 1% ozone in oxygen at 120°C for 2 h. Finally, the zeolite was calcined in oxygen at 450°C for 2 h (heating rate 1°C/min). Afterwards, the zeolite was converted into its ammonium form (Si/Al = 16, Al/Na > 150) by threefold ion exchange with 1 M aqueous ammonium nitrate at 60°C for 1 h. The experiments with 2-methyl-5-phenyl-2-pentene oxide (**1b**) were performed with another batch of zeolite NH_4-beta (Si/Al = 13, Al/Na = 120), which was prepared according to a similar procedure to that described above. − Zeolite NaY (Si/Al = 2.7, Al/Na = 1.0) was kindly donated by Akzo. The zeolite was exchanged with 1 M aqueous ammonium nitrate at 80 C for 24 h resulting in $NaNH_4Y$ (Si/Al =

2.6, Al/Na = 2.9). − Montmorillonite K10 (Si/Al = 5.1, Al/Na = 45) was purchased from Fluka. The clay was washed with 1 M aqueous ammonium chloride at room temp. for 23 h to eliminate possible metal impurities (Si/Al = 4.9, Al/Na = 41).[23] − Nafion NR50 perfluorinated sulfonic acid resin was purchased from Fluka. − All solid catalysts, with the exception of Nafion, were pre-activated at 450°C in a calcination oven for 17−25 h (including heating up at 1°C/min) prior to use in the catalytic reactions. By this thermal treatment the ammonium forms of the solids were converted to their protic forms.

4-Phenyl-1-butene Oxide (1a): The MCPBA (95 g, 70% purity, 0.39 mol, corrected for purity) was dissolved in dichloromethane (900 ml). After separation of the water layer using a separating funnel, the organic layer was dried with anhydrous Na_2SO_4 (47 g) for 1 h. To this solution was added dropwise over 0.5 h a solution of 4-phenyl-1-butene (25 g, 0.19 mol) in 75 ml of dichloromethane at 5°C with magnetic stirring. The mixture was allowed to warm to room temp. and stirred for an additional night. Subsequently, the white precipitate was filtered off and washed with dichloromethane. To the combined filtrates was added saturated aqueous $NaHCO_3$ (200 ml) and 20 wt-% aqueous Na_2SO_3 (200 ml) after which the mixture was stirred overnight. During this treatment the excess of MCPBA was totally destroyed, which was confirmed by GC analysis. After separation of the water layer, the organic layer was successively washed with water and saturated aqueous $NaHCO_3$, and dried with anhydrous Na_2SO_4. After evaporation of the major part of the solvent, the residual liquid was distilled. The epoxide was obtained in 72% yield as a colourless oil with a purity of 98% (determined by GC), b.p. 108°C/13 Torr. − ^{1}H NMR (400 MHz): δ = 1.78−1.93 (m, 2 H), 2.46 (dd, *J* = 3 Hz, *J* = 5 Hz, 1 H), 2.70−2.86 (m, 3 H), 2.91−2.98 (m, 1 H), 7.12−7.34 (m, 5 H). − ^{13}C NMR (100 MHz): δ = 32.2, 34.3, 47.2, 51.8, 126.0, 128.4 (2×), 141.3. − MS; *m*/*z* (%): 148 (10) [M^+], 130 (20), 129 (12), 118 (31), 117 (93), 115 (26), 105 (17), 104 (47), 92 (19), 91 (100), 77 (12), 65 (26), 51 (14).

2-Methyl-5-phenyl-2-pentene Oxide (1b): The epoxide was obtained by epoxidation of the corresponding alkene with MCPBA according to the procedure described above. 2-Methyl-5-phenyl-2-pentene was prepared by a Wittig procedure from 3-phenylpropanal and the phosphonium salt made from isopropyl bromide and triphenylphosphane. A Teflon insert of 250 ml was charged with triphenylphosphane (59.3 g, 0.226 mol) and isopropyl bromide (28.8 g, 0.234 mol). After flushing with nitrogen, the insert was closed, placed in an autoclave and heated at 150°C for 22 h. This afforded isopropyltriphenylphosphonium bromide in the form of a crystalline solid, which was successively pulverised, thoroughly washed with diethyl ether to remove residual reactants, filtered and dried over P_2O_5 under vacuum. To a suspension of this isopropyltriphenylphosphonium bromide (68.6 g, 0.178 mol) in dry tetrahydrofuran (250 ml) was slowly added under nitrogen 120 ml of a 1.6 M *n*-butyllithium solution in hexane. The reaction was slightly exothermic and an intensely red solution was formed. Afterwards, a solution of 3-phenylpropanal (23.7 g, 0.177 mol) in dry tetrahydrofuran (75 ml) was added under nitrogen with cooling of the reaction mixture in an ice bath. After the addition was complete, the ice bath was removed and the reaction mixture was stirred under nitrogen at room temp. overnight. The mixture was poured into water and then extracted with tetrahydrofuran. After being dried, the combined organic layers were filtered through a short silica gel column. Evaporation of the solvent afforded crude 2-methyl-5-phenyl-2-pentene (yield 85%, purity 90%). − ^{1}H NMR (60 MHz): δ = 1.54 (s, 3 H), 1.66 (s, 3 H), 2.00−2.80 (m, 4 H), 4.91−5.24 (m, 1 H), 7.10 (s, 5 H). − MS; *m*/*z* (%): 160 (34) [M^+], 92 (31), 91 (72), 69 (100), 68 (16), 65 (14). − The crude alkene was epoxidised with MCPBA (molar ratio peroxyacid/alkene = 1.4) affording epoxide **1b** in 78% yield (based on amount of alkene, corrected for purity alkene) as a colourless oil with a purity of 99% (determined by GC), b.p. 108°C/9 Torr. − ^{1}H NMR (400 MHz): δ = 1.09 (s, 3 H), 1.24 (s, 3 H), 1.72−1.92 (m, 2 H), 2.64−2.86 (m, 3 H), 7.14−7.28 (m, 5 H). − ^{13}C NMR (100 MHz): δ = 18.6, 24.8, 30.8, 32.7, 58.4, 63.7, 126.0, 128.4 (2 ×), 141.4. − MS; *m*/*z* (%): 176 (6) [M^+], 133 (10), 118 (57), 117 (63), 115 (12), 105 (38), 104 (15), 103 (8), 92 (21), 91 (100), 85 (94), 79 (8), 78 (17), 77 (15), 72 (84), 71 (8), 65 (21), 59 (60), 57 (15), 51 (11), 43 (11).

4-(3-Methoxyphenyl)-1-butene Oxide (1c): The epoxide was obtained by epoxidation of the corresponding alkene with MCPBA according to the procedure described above. 4-(3-Methoxyphenyl)-1-butene was prepared by a Grignard procedure from 3-methoxybenzyl chloride and allyl bromide. A three-necked, round-bottomed flask equipped with a magnetic stirrer bar, an addition funnel, a reflux condenser fitted with a calcium chloride tube and a nitrogen inlet was charged with magnesium turnings (8.29 g, 0.341 mol), sodium-dried diethyl ether (100 ml) and a small crystal of iodine. The reaction was started by introduction into the flask of a part of a solution of 3-methoxybenzyl chloride (48.9 g, 0.312 mol) in dry diethyl ether (50 ml). As soon as the reaction had commenced, the remainder of this solution was added dropwise maintaining a gentle reflux of the reaction mixture. When the reaction became too vigorous, it was moderated by momentarily cooling in an ice bath. After the addition was complete, the reaction mixture was stirred in an oil bath of 60°C to complete the formation of the Grignard reagent (approx. 10 min). Then a solution of allyl bromide (44.0 g, 0.364 mol) in dry diethyl ether (100 ml) was added over a period of 20 min, maintaining a gentle reflux by cooling of the flask in a water bath. The addition resulted in the formation of a precipitate. After heating the reaction mixture in an oil bath of 60°C for 20 min and cooling to room temp., water (200 ml) and some extra diethyl ether were added, which was followed by stirring of the mixture until a clear two-layer system was formed. After separation, the water layer was extracted with diethyl ether (2 × 200 ml). The combined organic layers were successively washed with water and saturated aqueous NaCl, and dried with anhydrous Na_2SO_4. Evaporation of the solvent afforded crude 4-(3-methoxyphenyl)-1-butene (yield 97%, purity 89%). − ^{1}H NMR (60 MHz): δ = 2.00−3.00 (m, 4 H), 3.66 (s, 3 H), 4.70−5.15 (m, 2 H), 5.44−6.10 (m, 1 H), 6.43−7.24 (m, 4 H). − MS; *m*/*z* (%): 162 (83) [M^+], 147 (8), 121 (100), 91 (13). − The crude alkene was epoxidised with MCPBA (molar ratio peroxyacid/alkene = 2.2) affording epoxide **1c** in 57% yield (based on amount of alkene, corrected for purity alkene) as a colourless oil with a purity of 97% (determined by GC), b.p. 86°C/0.1 Torr. − ^{1}H NMR (400 MHz): δ = 1.76−1.92 (m, 2 H), 2.46 (dd, *J* = 3 Hz, *J* = 5 Hz, 1 H), 2.66−2.84 (m, 3 H), 2.90−2.98 (m, 1 H), 3.77 (s, 3 H), 6.73 (d, *J* = 8 Hz, 1 H), 6.75 (s, 1 H), 6.79 (d, *J* = 8 Hz, 1 H), 7.19 (t, *J* = 8 Hz, 1 H). − ^{13}C NMR (100 MHz): δ = 32.3, 34.2, 47.2, 51.7, 55.1, 111.3, 114.2, 120.7, 129.4, 142.9, 159.7. − MS; *m*/*z* (%): 178 (92) [M^+], 159 (23), 148 (32), 147 (100), 135 (25), 134 (61), 122 (44), 121 (93), 117 (34), 91 (76), 78 (36), 77 (38), 65 (27).

5-(3-Methoxyphenyl)-2-pentene Oxide (1d, *trans*/*cis* = 3.89): The epoxide was obtained by epoxidation of the corresponding alkene with MCPBA as described earlier. 5-(3-methoxyphenyl)-2-pentene was prepared from 3-methoxybenzyl chloride and crotyl bromide according to the Grignard procedure described above. In this way, an isomeric mixture of products was obtained which was used without further purification in the epoxidation reaction. The reaction product from the epoxidation was subjected to careful column

chromatography (EtOAc/hexane = 1:10) to afford a *trans*/*cis* mixture of epoxide **1d** in a ratio of 3.89 (determined by GC) and with a purity of 90% (determined by GC). − GC analysis: t_r(*trans*) < t_r(*cis*). − ^{1}H NMR (400 MHz): δ = 1.19 (d, *J* = 5 Hz, 0.6 H, *cis*-CH_3), 1.25 (d, *J* = 5 Hz, 2.4 H, *trans*-CH_3), 1.74−1.92 (m, 2 H), 2.61−3.06 (m, 4 H), 3.79 (s, 3 H), 6.70−6.82 (m, 3 H), 7.16−7.26 (m, 1 H). − ^{13}C NMR (100 MHz): δ = 13.1, 17.6, 29.4, 32.3, 32.8, 33.8, 52.8, 54.8, 55.1, 56.5, 59.1, 111.3, 114.2, 114.3, 120.8, 129.4, 143.0, 159.7. − MS; *m*/*z* (%): *trans*: 192 (79) [M^+], 174 (16), 161 (37), 159 (40), 148 (57), 147 (63), 137 (41), 135 (34), 134 (100), 133 (21), 122 (32), 121 (74), 117 (43), 115 (18), 109 (16), 105 (23), 91 (53), 78 (24), 77 (29), 71 (20), 65 (20), 45 (45), 43 (28). − MS; *m*/*z* (%): *cis*: 192 (100) [M^+], 177 (12), 159 (26), 149 (18), 148 (77), 147 (93), 137 (60), 135 (60), 134 (99), 133 (28), 122 (37), 121 (86), 117 (66), 116 (18), 115 (20), 109 (19), 105 (31), 103 (15), 91 (61), 79 (15), 78 (30), 77 (36), 71 (29), 65 (25), 51 (16), 45 (66), 43 (46).

5-(3-Methoxyphenyl)-2-methyl-2-pentene Oxide (1e): The epoxide was obtained by epoxidation of the corresponding alkene with MCPBA as described earlier. 5-(3-Methoxyphenyl)-2-methyl-2-pentene was prepared from 3-methoxybenzyl chloride and 3,3-dimethylallyl bromide according to the Grignard procedure described above. In this way, an isomeric mixture of products was obtained which was used without further purification in the epoxidation reaction. The reaction product from the epoxidation was subjected to careful column chromatography (EtOAc/hexane = 1:20) to afford epoxide **1e** with a purity of 91% (determined by GC). − ^{1}H NMR (60 MHz): δ = 1.11 (s, 3 H), 1.23 (s, 3 H), 1.56−2.05 (m, 3 H), 2.48−3.01 (m, 3 H), 3.72 (s, 3 H), 6.52−6.82 (m, 3 H), 6.93−7.31 (m, 1 H). − MS; *m*/*z* (%): 206 (63) [M^+], 148 (49), 147 (77), 135 (64), 134 (100), 122 (65), 121 (79), 117 (58), 91 (44), 85 (70), 77 (25), 59 (62).

Remarks: Although the synthesis of 4-(3-methoxyphenyl)-1-butene oxide according to the Grignard procedure described above afforded a high yield, we encountered serious difficulties with the synthesis of 5-(3-methoxyphenyl)-2-pentene oxide and 5-(3-methoxyphenyl)-2-methyl-2-pentene oxide. In both cases, product mixtures (in high overall yields!) comprising various isomers were obtained, resulting finally in low yields of the desired products. For the former alkene this could be partially explained by 3-bromo-1-butene as a major impurity (15%) in the commercially purchased crotyl bromide. Moreover, these substituted allyl bromides appeared to be prone to attack of the Grignard reagent at the double bond, followed by bromide elimination. Since Grignard reagents may be in equilibrium with magnesium halides and dialkylmagnesium compounds, and magnesium halides (Lewis acids) can cause prior isomerisation of a substrate[24], it is not unlikely that the double bond attack is catalysed by $MgCl_2$. A possible involvement of this Lewis acid and MgBrCl, which is formed during the reaction, is in agreement with the higher susceptibility to double bond attack of the substituted allyl bromides, since electron-releasing substituents are expected to favour Lewis acid catalysed additions to these bonds.

Catalytic Reactions with Solid Acids: The reactions were carried out in a 250-ml three-necked, round-bottomed flask equipped with a magnetic stirrer bar and a condenser fitted with a calcium chloride tube. The solid acid, pre-activated (450°C, overnight), was suspended in a solution of the epoxide and 1,3,5-tri-*tert*-butylbenzene in benzene. The reaction mixture was heated to the desired temp. with stirring at 1000 rpm. Aliquots were taken during the reaction and analysed by GC. Products were isolated by column chromatography and identified by NMR and GC/MS.

Identification of the Reaction Products: After the completion of the catalytic experiments, the various products were isolated from the reaction mixtures by removal of the solid catalyst (by filtration or centrifugation) and solvent (evaporation), followed by purification (column chromatography). The purest fractions, containing preferentially a single component, were collected and subjected to further identification. In some cases, reactions on a larger scale were performed, without the presence of internal standard, to obtain a larger amount of a product.

1,2,3,4-Tetrahydro-2-naphthol (2a): Isolated from the reaction product by column chromatography with EtOAc/hexane = 3:10 as an eluent [TLC: R_f(**2a**) ≈ 0.15]. − ^{1}H NMR (300 MHz): δ = 1.71−1.87 (m, 1 H), 1.97−2.16 (m, 2 H), 2.62−3.12 (m, 4 H), 4.06−4.18 (m, 1 H), 7.00−7.15 (m, 4 H). − ^{13}C NMR (75 MHz): δ = 27.0 (CH_2CH_2CHOH), 31.5 (ArCH_2CH_2), 38.4 (ArCH_2-CHOH), 67.2 (COH), 125.8 (Ar CH), 125.9 (Ar CH), 128.6 (Ar CH), 129.5 (Ar CH), 134.3 (Ar C), 135.7 (Ar C). − MS; *m*/*z* (%): 148 (14) [M^+], 131 (14), 130 (100), 129 (34), 115 (26), 105 (19), 104 (75), 103 (18), 91 (19), 78 (20), 77 (14).

Cyclialkylation and Rearrangement Products from 2-Methyl-5-phenyl-2-pentene Oxide (1b): The various products were identified by GC/MS. Compounds **2b**, **4**, **5** and **6** were also isolated from the reaction product by column chromatography with gradient elution. The chromatography process was first performed with EtOAc/hexane = 1:20 as an eluent, then with EtOAc/hexane = 1:5 and finally with EtOAc/hexane = 1:1. In this way, pure fractions of each compound were obtained. − GC: t_r(**4**) < t_r(**5**) < t_r(**8**) < t_r(**6**) < t_r(**2b**) < t_r(**7**).

1,1-Dimethyl-1,2,3,4-tetrahydro-2-naphthol (2b): ^{1}H NMR (300 MHz): δ = 1.24 (s, 3 H), 1.30 (s, 3 H), 1.80−2.00 (m, 2 H), 2.42 (br. s, 1 H, OH), 2.70−2.96 (m, 2 H), 3.67 (dd, *J* = 3 Hz, *J* = 9 Hz, 1 H), 6.98−7.16 (m, 3 H), 7.30 (dd, *J* = 1 Hz, *J* = 8 Hz, 1 H). − ^{13}C NMR (75 MHz): δ = 25.0 (CH_3), 26.8 (CH_2), 27.1 (CH_2), 28.9 (CH_3), 39.0 (Ar*C*CHOH), 75.5 (COH), 125.6 (Ar CH), 126.1 (Ar CH), 126.8 (Ar CH), 128.7 (Ar CH), 134.5 (Ar C), 144.3 (Ar C). − MS; *m*/*z* (%): 176 (7) [M^+], 161 (19), 159 (12), 158 (72), 144 (19), 143 (100), 133 (14), 132 (64), 131 (20), 129 (15), 128 (30), 119 (25), 117 (63), 116 (15), 115 (34), 105 (10), 92 (10), 91 (43), 77 (12), 51 (9), 43 (9).

3-Methyl-5-phenyl-2-pentanone (4): Both the ^{1}H-NMR spectrum and ^{13}C-NMR spectrum were very complex, suggesting the presence of more than one product. Conversely, GC analysis showed only one peak for the isolated product and identical mass spectra were reproducibly obtained for this peak in different reactions. Furthermore, the mass spectrum fragmentation pathway was in agreement with the assigned structure. Careful interpretation of the NMR spectra leads us to suspect that product **4** was predominantly present in its two possible enolic forms, resulting in singlets at δ = 1.09, 1.26 and 1.51 for the methyl groups (^{1}H-NMR spectrum). Moreover, these enolic forms may explain the occurrence of the ^{13}C signals at δ = 160.6 and 184.1, in addition to the carbonyl signal at δ = 205.9. − MS; *m*/*z* (%): 176 (3) [M^+], 105 (21), 104 (16), 92 (15), 91 (97), 77 (6), 73 (5), 72 (100), 65 (14), 57 (11), 51 (6), 43 (5).

2-Methyl-5-phenyl-3-pentanone (5): ^{1}H NMR (300 MHz): δ = 1.04 (d, *J* = 7 Hz, 6 H), 2.53 (sept, *J* = 7 Hz, 1 H), 2.74 (t, *J* = 7 Hz, 2 H), 2.87 (t, *J* = 7 Hz, 2 H), 7.10−7.30 (m, 5 H). − ^{13}C NMR (75 MHz): δ = 18.1, 29.8, 40.9, 41.9, 126.0, 128.3, 128.4, 141.3, 213.5. − MS; *m*/*z* (%): 176 (24) [M^+], 133 (42), 105 (99), 91 (100), 77 (16), 43 (50).

3-Hydroxy-2-methyl-5-phenyl-1-pentene (6): ^{1}H NMR (300 MHz): δ = 1.72 (s, 3 H), 1.84 (dt, *J* = 6 Hz, *J* = 8 Hz, 2 H), 1.98 (br. s, 1 H, OH), 2.55−2.77 (m, 2 H), 4.06 (t, *J* = 6 Hz, 1 H), 4.85 (br. s, 1 H), 4.95 (br. s, 1 H), 7.13−7.21 (m, 3 H), 7.23−7.30 (m, 2 H).

− ^{13}C NMR (75 MHz): δ = 17.6, 31.9, 36.5, 75.2, 111.2, 125.8, 128.3, 128.4, 142.0, 147.4. − MS; *m*/*z* (%): 176 (39) [M$^+$], 158 (17), 143 (47), 129 (20), 105 (58), 104 (25), 92 (62), 91 (100), 85 (17), 79 (18), 78 (25), 77 (22), 72 (77), 71 (81), 65 (23), 43 (27).

2-Hydroxy-2-methyl-5-phenyl-3-pentene (7): MS; *m*/*z* (%): 176 (2) [M$^+$], 161 (3), 136 (14), 118 (21), 117 (8), 105 (11), 104 (4), 92 (31), 91 (54), 90 (5), 79 (4), 78 (5), 77 (7), 72 (16), 65 (12), 60 (5), 59 (100), 51 (6), 43 (15).

2-Methyl-5-phenyl-2,4-pentadiene (8): MS; *m*/*z* (%): 158 (52) [M$^+$], 143 (100), 141 (21), 129 (21), 128 (50), 115 (22).

Cyclialkylation Products from 4-(3-Methoxyphenyl)-1-butene Oxide (1c): Tetrahydronaphthols **2c** and **3c** were isolated from the reaction product by column chromatography with EtOAc/hexane = 3:10 as an eluent [TLC: R_f(**2c**) < R_f(**3c**)]. − GC: t_r(**2c**) > t_r(**3c**).

6-Methoxy-1,2,3,4-tetrahydro-2-naphthol (2c): ^{1}H NMR (400 MHz): δ = 1.61 (br. s, 1 H, OH), 1.75−1.86 (m, 1 H), 1.99−2.08 (m, 1 H), 2.70 (dd, *J* = 8 Hz, *J* = 16 Hz, 1 H), 2.77−2.98 (m, 2 H), 3.03 (dd, *J* = 5 Hz, *J* = 16 Hz, 1 H), 3.77 (s, 3 H), 4.11−4.18 (m, 1 H), 6.64 (d, *J* = 3 Hz, 1 H), 6.71 (dd, *J* = 3 Hz, *J* = 8 Hz, 1 H), 7.00 (d, *J* = 8 Hz, 1 H). − ^{13}C NMR (100 MHz): δ = 27.3 (CH$_2$*C*H$_2$CHOH), 31.4 (Ar*C*H$_2$CH$_2$), 37.6 (Ar*C*H$_2$CHOH), 55.2 (OCH$_3$), 67.4 (COH), 112.2 (Ar CH), 113.2 (Ar CH), 126.3 (Ar C), 130.3 (Ar CH), 136.8 (Ar C), 157.8 (Ar C). − MS; *m*/*z* (%): 178 (59) [M$^+$], 160 (54), 159 (20), 150 (16), 145 (14), 135 (29), 134 (100), 121 (20), 115 (14), 104 (17), 91 (33), 77 (17), 65 (13), 51 (13).

8-Methoxy-1,2,3,4-tetrahydro-2-naphthol (3c): ^{1}H NMR (400 MHz): δ = 1.70−1.80 (m, 1 H), 1.93−2.01 (m, 1 H), 2.48−2.57 (m, 2 H), 2.72−2.98 (m, 2 H), 3.05 (dd, *J* = 5 Hz, *J* = 17 Hz, 1 H), 3.77 (s, 3 H), 4.04−4.12 (m, 1 H), 6.63 (d, *J* = 8 Hz, 1 H), 6.69 (d, *J* = 8 Hz, 1 H), 7.07 (t, *J* = 8 Hz, 1 H). − ^{13}C NMR (100 MHz): δ = 27.1 (CH$_2$*C*H$_2$CHOH), 30.9 (Ar*C*H$_2$CH$_2$), 32.3 (Ar*C*H$_2$CHOH), 55.1 (OCH$_3$), 67.1 (COH), 107.0 (Ar CH), 120.8 (Ar CH), 123.2 (Ar C), 126.2 (Ar CH), 137.1 (Ar C), 157.5 (Ar C). − MS; *m*/*z* (%): 178 (96) [M$^+$], 160 (100), 159 (64), 150 (30), 147 (34), 145 (47), 135 (41), 134 (79), 129 (39), 121 (29), 115 (37), 105 (30), 104 (87), 103 (32), 91 (61), 78 (29), 77 (32), 65 (25).

Cyclialkylation Products from 5-(3-Methoxyphenyl)-2-pentene Oxide (1d): Tetrahydronaphthols **2d** and **3d** were isolated from the reaction product by column chromatography with EtOAc/hexane = 1:5 as an eluent [TLC: R_f(**2d**) < R_f(**3d**)]. Both compounds were obtained as *trans*/*cis* mixtures in ratios of 3.03 and 13.2, respectively (determined by GC). − GC: t_r(**2d**, *cis*) > t_r(**2d**, *trans*) > t_r(**3d**, *cis*) > t_r(**3d**, *trans*).

6-Methoxy-1-methyl-1,2,3,4-tetrahydro-2-naphthol (2d, *trans*/*cis* = 3.03): ^{1}H NMR (400 MHz): δ = 1.25 (d, *J* = 7 Hz, 0.75 H, *cis*-CH$_3$), 1.30 (d, *J* = 7 Hz, 2.25 H, *trans*-CH$_3$), 1.76−2.06 (m, 2 H), 2.07 (br. s, 1 H, OH), 2.70−3.06 (m, 3 H), 3.62−3.82 (m, 0.75 H, *trans*), 3.76 (s, 3 H), 4.05−4.14 (m, 0.25 H, *cis*), 6.61 (d, *J* = 2 Hz, 1 H), 6.73 (dd, *J* = 3 Hz, *J* = 9 Hz, 1 H), 7.08 (d, *J* = 9 Hz, 0.25 H, *cis*), 7.11 (d, *J* = 9 Hz, 0.75 H, *trans*). − ^{13}C NMR (100 MHz): *trans*: δ = 20.4 (CH$_3$), 26.4 (CH$_2$), 28.2 (CH$_2$), 40.4 (Ar*C*H), 55.1 (OCH$_3$), 72.5 (COH), 112.4 (Ar CH), 113.0 (Ar CH), 129.6 (Ar CH), 131.8 (Ar C), 136.6 (Ar C), 157.5 (Ar C). − ^{13}C NMR (100 MHz): *cis*: δ = 16.7 (CH$_3$), 27.0 (CH$_2$), 27.5 (CH$_2$), 37.8 (Ar*C*H), 55.1 (OCH$_3$), 70.1 (COH), 112.3 (Ar CH), 113.0 (Ar CH), 129.7 (Ar CH), 132.7 (Ar C), 136.3 (Ar C), 157.6 (Ar C). − MS; *m*/*z* (%): *trans*: 192 (70) [M$^+$], 177 (35), 174 (23), 159 (45), 149 (25), 148 (100), 147 (21), 135 (20). − MS; *m*/*z* (%): *cis*: 192 (60) [M$^+$], 177 (33), 174 (21), 159 (39), 149 (30), 148 (100), 147 (23), 135 (26).

8-Methoxy-1-methyl-1,2,3,4-tetrahydro-2-naphthol (3d, *trans*/*cis* = 13.2): ^{1}H NMR (400 MHz): δ = 1.17 (d, *J* = 7 Hz, 3 H), 1.56 (br. s, 1 H, OH), 1.85−2.03 (m, 2 H), 2.72 (ddd, *J* = 2 Hz, *J* = 6 Hz, *J* = 17 Hz, 1 H), 2.93−3.04 (m, 1 H), 3.14 (br. q, *J* = 7 Hz, 1 H), 3.82 (s, 3 H), 4.01−4.06 (m, 1 H), 6.68 (d, *J* = 8 Hz, 1 H), 6.72 (d, *J* = 8 Hz, 1 H), 7.09 (t, *J* = 8 Hz, 1 H). − ^{13}C NMR (100 MHz): *trans*: δ = 19.7 (CH$_3$), 23.5 (CH$_2$), 24.0 (CH$_2$), 35.1 (Ar*C*H), 54.9 (OCH$_3$), 70.6 (COH), 107.3 (Ar CH), 121.1 (Ar CH), 126.0 (Ar CH), 127.5 (Ar C), 136.3 (Ar C), 157.8 (Ar C). − MS; *m*/*z* (%): *trans*: 192 (69) [M$^+$], 177 (22), 174 (38), 160 (20), 159 (100), 148 (27), 144 (20), 135 (32), 133 (61), 115 (28), 105 (37), 91 (22). − MS; *m*/*z* (%): *cis*: 192 (65) [M$^+$], 174 (42), 159 (100), 144 (15), 135 (26), 134 (45), 133 (18), 115 (18), 105 (20), 104 (38), 91 (25).

Cyclialkylation Products from 5-(3-Methoxyphenyl)-2-methyl-2-pentene Oxide (1e): Tetrahydronaphthols **2e** and **3e** and rearrangement products **9** and **10** were isolated from the reaction product by column chromatography with EtOAc/hexane = 1:8 as an eluent [TLC: R_f(**2e**) < R_f(**3e**) < R_f(**9**+**10**)]. − GC: t_r(**2e**) > t_r(**3e**) > t_r(**9**+**10**). Compounds **9** and **10** were obtained as a mixture in a ratio of 2 (determined by NMR). GC analysis of this mixture gave exactly overlapping peaks both on CP Sil 5 CB and CP Wax 52 CB columns.

6-Methoxy-1,1-dimethyl-1,2,3,4-tetrahydro-2-naphthol (2e): ^{1}H NMR (300 MHz): δ = 1.23 (s, 3 H), 1.29 (s, 3 H), 1.80−2.04 (m, 2 H), 2.17 (br. s, 1 H, OH), 2.72−2.96 (m, 2 H), 3.69 (dd, *J* = 3 Hz, *J* = 9 Hz, 1 H), 3.73 (s, 3 H), 6.56 (d, *J* = 3 Hz, 1 H), 6.73 (dd, *J* = 3 Hz, *J* = 9 Hz, 1 H), 7.23 (d, *J* = 9 Hz, 1 H). − ^{13}C NMR (75 MHz): δ = 25.1 (CH$_3$), 26.9 (CH$_2$), 27.3 (CH$_2$), 29.0 (CH$_3$), 38.5 (Ar*C*), 55.1 (OCH$_3$), 75.5 (COH), 112.6 (Ar CH), 112.9 (Ar CH), 127.9 (Ar CH), 135.8 (Ar C), 136.6 (Ar C), 157.3 (Ar C). − MS; *m*/*z* (%): 206 (49) [M$^+$], 191 (100), 173 (37), 162 (52), 147 (35), 121 (19).

8-Methoxy-1,1-dimethyl-1,2,3,4-tetrahydro-2-naphthol (3e): ^{1}H NMR (300 MHz): δ = 1.38 (s, 3 H), 1.42 (s, 3 H), 1.78−1.97 (m, 2 H), 2.04 (br. s, 1 H, OH), 2.70−3.00 (m, 2 H), 3.63 (dd, *J* = 3 Hz, *J* = 8 Hz, 1 H), 3.78 (s, 3 H), 6.67 (d, *J* = 8 Hz, 1 H), 6.68 (d, *J* = 8 Hz, 1 H), 7.05 (t, *J* = 8 Hz, 1 H). − ^{13}C NMR (75 MHz): δ = 21.4 (CH$_3$), 26.1 (CH$_3$), 26.5 (CH$_2$), 27.9 (CH$_2$), 38.8 (Ar*C*), 55.0 (OCH$_3$), 77.3 (COH), 109.3 (Ar CH), 121.7 (Ar CH), 126.4 (Ar CH), 132.3 (Ar C), 137.1 (Ar C), 159.3 (Ar C). − MS; *m*/*z* (%): 206 (66) [M$^+$], 191 (79), 188 (26), 173 (100), 158 (23), 149 (30), 147 (47), 119 (20), 115 (19), 91 (19).

Mixture of 5-(3-Methoxyphenyl)-2-methyl-3-pentanone (9) and 4-(3-Methoxyphenyl)-2,2-dimethylbutanal (10) [Ratio 9/10 = 2 (Determined by NMR)]: ^{1}H NMR (300 MHz): δ = 1.07 (d, *J* = 7 Hz, 4 H, **9** CH$_3$), 1.12 (s, 2 H, **10** CH$_3$), 1.73−1.82 (m, 0.66 H, **10** CH$_2$), 2.45−2.62 (m, 1.33 H), 2.72−2.91 (m, 2.66 H), 3.78 (s + s, 3 H), 6.68−6.80 (m, 3 H), 7.14−7.27 (m, 1 H), 9.47 (s, 0.33 H, **10** CHO). − ^{13}C NMR (75 MHz): δ = 18.1 (CH$_3$), 21.4 (CH$_3$), 29.9 (CH$_2$), 30.8 (CH$_2$), 39.1 (CH$_2$), 41.0 (**9** *C*HC=O), 41.9 (CH$_2$), 45.9 (**10** *C*CHO), 55.1 (OCH$_3$), 111.3 (Ar CH), 111.4 (Ar CH), 114.1 (Ar CH), 120.7 (Ar CH), 129.4 (Ar CH), 143.0 (Ar C), 143.5 (Ar C), 159.7 (Ar C), 205.8 (**10** CHO), 213.6 (**9** C=O).

Acknowledgments

The work described in this paper was financially supported by the Dutch Innovation Oriented Research Programme on Catalysis (IOP Catalysis).

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Received September 9, 1998
[O98402]