

Reactions of Allyl Phenyl Ether in High-Temperature Water with Conventional and Microwave Heating

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Received June 11, 1996[⊙]

In a systematic study, allyl phenyl ether (**1**) was heated in water for 1 h at temperatures of 180 °C and above. Parallel experiments were conducted with a conventionally heated autoclave and a recently developed microwave batch reactor. Relatively modest temperature differences resulted in diverse product distributions, and these were independent of the method of heating. Maximum conversion of **1** to 2-allylphenol occurred at 200 °C (56%) and to 2-methyl-2,3-dihydrobenzofuran at 250 °C (72%). Although 2-(2-hydroxyprop-1-yl)phenol comprised less than 1% of the product mixture at both 180 and 260 °C, it accounted for 37% at 230 °C. The reaction sequence was investigated by heating intermediates individually at selected temperatures up to 290 °C. Hydration of 2-allylphenol to 2-(2-hydroxyprop-1-yl)phenol was partially reversible. The work showed that high-temperature water constitutes an environmentally benign alternative to the use of acid catalysts or organic solvents and offers scope for interconversion of alcohols and alkenes.

Introduction

When temperatures in the order of 200 °C or above are required for organic reactions, the choice of solvents is limited. We have achieved such temperatures through heating of low-boiling solvents under pressure in conventional autoclaves and with novel, specifically designed microwave reactors.^{1–3} This methodology has the advantages that high reaction rates can be obtained, the products can be easily isolated, and the solvent can often be recovered for reuse if desired.

However, safety, economic, and environmental considerations⁴ dictate the need for decreased usage of organic solvents in chemical laboratories and in industrial processes. The phasing out of some halogenated solvents, particularly chlorofluorocarbons and CCl₄,⁵ and the search for suitable replacement media⁶ are indicative of the trend.

Along with others,^{7–10} we have found that high-temperature water can be beneficial for synthetic reactions, since it behaves as a pseudoorganic solvent.^{3,11}

Apart from the environmental benefits of replacing organic solvents with water, the solubility of organic material will normally diminish with cooling of completed reactions, thereby facilitating workup.

Two of us recently reported preliminary results for the microwave-assisted reaction of allyl phenyl ether (**1**) in water.³ At 240 °C, within 10 min, 2-allylphenol (**2**) was obtained almost exclusively and in high conversion, but at 250 °C participation of water became apparent. These findings encouraged us to study the reaction systematically. Three broad aims of this work were to determine reaction pathways of **1** in high-temperature water, to explore applications of high-temperature water as a medium for environmentally benign organic chemistry, and to attempt the translation of conditions between microwave-assistance and conventional heating for a relatively complex system.

Results

Experiments were conducted in a microwave batch reactor (MBR)¹ that was operable up to 260 °C and a commercial conventionally heated autoclave that could accommodate temperatures above 300 °C. The autoclave had considerable thermal inertia, owing to its high mass, and consequently, heating times were relatively slow.³ Therefore, to avoid erroneous results, water was preheated to the designated temperature, and the starting material was then injected under pressure of argon. Since reactions could be heated within a few minutes in the MBR, aqueous mixtures of the starting material were merely added to the vessel under an argon atmosphere at ambient temperature and then taken to the required temperature.

Reactions of Allyl Phenyl Ether (1). Mixtures of **1** in water were heated in the autoclave and the MBR for 1 h and then rapidly cooled. The products were extracted and analyzed. Compounds quantified were 2-allylphenol (**2**), phenol (**3**), *cis*- and *trans*-2-(prop-1-enyl)phenols (**4** and **5**, respectively), 2-(2-hydroxyprop-1-yl)phenol (**6**), and 2-methyl-2,3-dihydrobenzofuran (**7**). There were differences (discussed below) between corresponding sets of data from reactions in the microwave and autoclave, but the course of conversion of starting ether **1** was consistent

[⊙] Abstract published in *Advance ACS Abstracts*, September 15, 1996.

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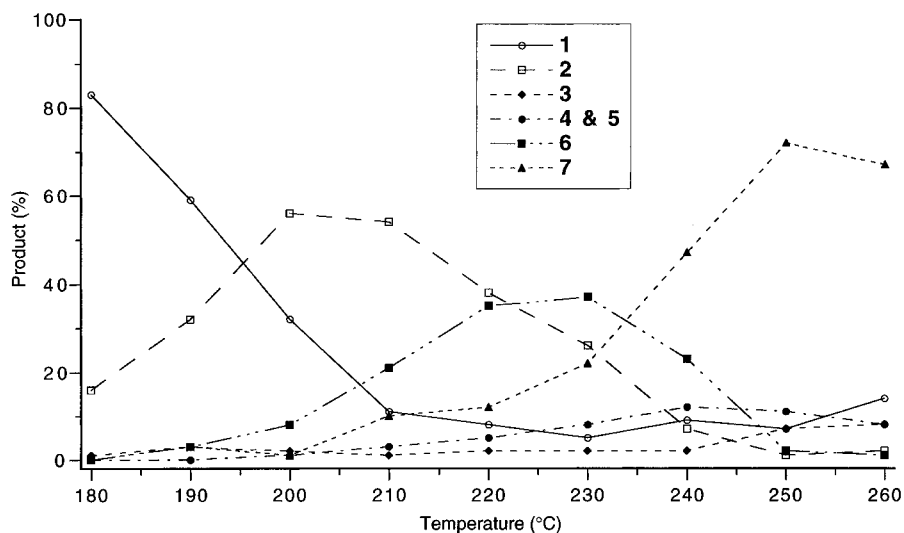


Figure 1. Products obtained from reaction of allyl phenyl ether (**1**) in the MBR. Product ratios were estimated by ^1H NMR.

for both heating methods. The percentage composition of the extracts from MBR experiments is plotted against reaction temperature in Figure 1.

From Figure 1, ether **1** was converted in approximately equal increments between 180 and 210 °C, but at higher temperatures the gradient of the curve altered significantly. At 230 °C, the proportion of unreacted **1** attained a minimum of 5%, but surprisingly, from there the conversion was lower. Up to 190 °C, *ortho*-Claisen rearrangement occurred almost exclusively, the maximum conversion to **2** being 56% at 200 °C. Beyond 190 °C, five products were detected: phenol (**3**), prop-1-enylphenols **4** and **5**, hydroxyphenol **6**, and dihydrobenzofuran **7**. The concentration of **3** was 3% or less at temperatures up to 240 °C but gradually increased with further rises in reaction temperature, attaining 9% at 260 °C. Phenol (**3**) and allyl alcohol, which was expected but was not detected under the analytical conditions, may have been formed directly from **1** through aqueous substitution at C-1 or C-3 of the allyl side chain.

The maximum conversion of **1** to hydroxyphenol **6** was 37% at 230 °C. However, **6** was observed in only trace amounts at 180 °C and comprised only *ca.* 1% of the product mixture at 260 °C. This highlighted benefits of a systematic study employing small increments in temperature. It also suggested that **6** was formed by addition of water to 2-allylphenol (**2**) at and above 190 °C but also underwent conversion to other products, particularly above 230 °C. Hence, water not only served as the medium for reaction, but also participated.

Of the other products, 2-methyl-2,3-dihydrobenzofuran (**7**) and the isomeric 2-(prop-1-enyl)phenols **4** and **5** were minor constituents below 200 °C, and their abundance increased with temperature. At and above 240 °C, dihydrofuran **7** was clearly the major product, its concentration increasing sharply from 220 °C, before reaching a peak of 72% at 250 °C.

Reactions of Intermediates and/or Products. The above results suggested that equilibria existed between some of the products, and this was investigated by heating 2-allylphenol (**2**), *trans*-2-(prop-1-enyl)phenol (**5**), 2-(2-hydroxyprop-1-yl)phenol (**6**), and 2-methyl-2,3-dihydrobenzofuran (**7**) individually in high-temperature water for 1 h in the autoclave (Table 1).

2-Allylphenol (**2**) was relatively slow to react, even at 290 °C. At 200 °C and 250 °C, total conversions were

Table 1. Products from Reactions of 1, 2, 5, 6, and 7 (Autoclave)

entry no.	reactant	T (°C)	products (conversion, %) ^a						
			1	2	3	4	5	6	7
1	1	250	2	18	2	3	11	28	36
2	1	290	1	6	6	25			62
3	1	290 ^b		87	3	1	2		7
4	2	200		84			1	13	2
5	2	250		70	1		1	25	3
6	2	290		49	1	2	7	24	17
7	2	290 ^c		5	5	6	20		64
8	5	250		3	6	18	67		6
9	5	290			8	15	44		33
10	6	250		8	2		1	86	3
11	6	290		21	4	5	19	23	28
12	7	290							100
13	7	290 ^c			6	1	5		88

^a Estimated by ^1H NMR. ^b Neat. ^c pH adjusted to 3.2 with H_2SO_4 prior to reaction.

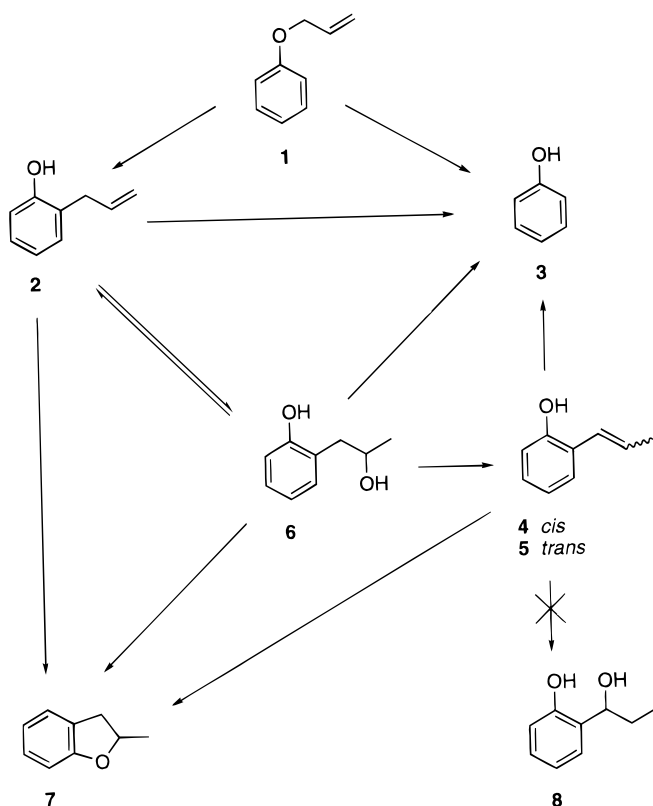
only 16% and 30%, respectively, with hydroxyphenol **6** being the major product formed (entries 4 and 5, Table 1). Although the conversion of **2** increased to 51% at 290 °C (entry 6, Table 1) and hydroxyphenol **6** remained the major product, dihydrofuran **7** and the isomeric phenols **4** and **5** also became significant constituents, with phenol (**3**) detected at a low level.

The treatment of *trans*-2-(prop-1-enyl)phenol (**5**) at 250 °C afforded mainly the corresponding *cis*-isomer **4** but also gave phenol (**3**) and dihydrofuran (**7**) in lesser amounts (entry 8, Table 1). At 290 °C, conversion of **5** to dihydrofuran **7** clearly predominated, even though *cis*-isomer **4** and phenol (**3**) remained components (entry 9, Table 1). Hydroxyphenol **6** or 2-(1-hydroxypropyl)phenol (**8**), possible hydration products of **5**, were not observed at either temperature. Furthermore, rearrangement to allylphenol **2** was only observed at 250 °C, and even then, as a minor transformation.

Hydroxyphenol **6** was relatively stable at 250 °C, affording allylphenol **2** as the major product, but in only 8% conversion (entry 10, Table 1). At 290 °C, **6** gave an array of compounds, including dihydrofuran **7** (28% conversion), allylphenol **2**, and propenylphenols **4** and **5** (entry 11, Table 1). Of the dehydration products, **2** was clearly favored at 250 °C, and remained significant at 290 °C, although the conversion was low in both cases.

Finally, dihydrobenzofuran **7** was unreactive within 1 h in water at 290 °C (entry 12, Table 1). In dilute H_2SO_4

Scheme 1. Reaction Pathways of Allyl Phenyl Ether (1) in High-Temperature Water



at 290 °C, however, **7** partially underwent ring opening to afford propenylphenols **4** and **5** and phenol (**3**), but in total conversion of only 12% (entry 13, Table 1).

Discussion

In a prior study of the *ortho*-Claisen rearrangement, White *et al.*¹² converted **1** to 2-allylphenol (**2**) in good yield by refluxing the neat ether for several hours. Subsequently, Svanholm and Parker¹³ discovered that allyl phenyl ethers spontaneously rearranged at room temperature in TFA. The rate of reaction at 60 °C was estimated to be orders of magnitude faster than that for the same compound in other solvents. Closer examination led Widmer *et al.*¹⁴ to conclude that reactions in TFA had little preparative value, owing to the formation of byproducts including phenol (**3**) and hydroxyphenol **6** in the acidic medium and also to facile ring closure of 2-allylphenol (**2**) to give 2-methyl-2,3-dihydrobenzofuran (**7**).

More recently, in studies of the Claisen rearrangement of allyl vinyl ethers, the advantages of water were first demonstrated.¹⁵ Rearrangements at temperatures below boiling were promoted through hydrophobic effects brought about by the tendency of nonpolar species to aggregate in water solution so as to decrease the hydrocarbon-water interfacial area.¹⁶

In the present work, allyl phenyl ether was relatively unreactive in water at 180 °C in 1 h but was converted readily at higher temperatures (see Figure 1). The extent of *ortho*-Claisen rearrangement at around 200 °C was comparable with that obtained from the neat ether (bp 192 °C) at reflux for 6 h.¹² Clearly, since high temperatures were required before the reaction would proceed, and the rate was not significantly affected by the presence of water, hydrophobic effects were inconsequential.

However, in water at higher temperatures, **1** gave products in common with those reported in TFA at 60 °C.¹⁴ From Figure 1, the highest conversion of **1** to **2** was 56% at 200 °C, **1** to **6** was 37% at 230 °C, and **1** to **7** was 72% at 250 °C. Hence, relatively modest changes in temperature led to substantially different product distributions, even though conversions were not always high. In TFA, however, a comparable degree of control was not obtained.^{13,14} Obvious additional advantages of water over TFA as a reaction medium include lower cost and toxicity, as well as easier handling and disposal. Consistent with earlier findings for unrelated reactions, this work further illustrates that, for synthesis, high-temperature water can be an attractive alternative to the use of more aggressive solvents and/or catalysts at lower temperatures.³

Reaction Pathway. From Table 1, autoclave reactions confirmed the interconvertibility of allylphenol (**2**) and hydroxyphenol (**6**) in high-temperature water (entries 4–6, 10, and 11). Somewhat unexpectedly, hydration of propenylphenol **5** was not observed, but it would have been expected to afford hydroxyphenol **8** in preference to **6** (entries 8 and 9, Table 1). Furthermore, **5** isomerized to allylphenol **2** to only a minor extent, even though it underwent about a similar degree of conversion as **2** under comparable conditions. These results suggest that allylic migration of the side-chain double bond of **2** proceeded *via* the reversible addition of water to produce hydroxyphenol **6**, which could also eliminate water, to give **5**.

Hydration of the allylic double bond of **2** occurred at lower temperature and, thus, was kinetically favored over intramolecular cyclization that would have afforded **7** (entries 4 and 6, Table 1).^{14,17} Addition of water to **2** proceeded in Markovnikov fashion, consistent with an ionic mechanism as expected.⁷ Although the conversion to hydroxyphenol **6** was only moderate under the chosen conditions, the convenience of the procedure suggests that high-temperature water could find broader applications for preparation of alcohols from alkenes.¹⁸

On the other hand, although an aqueous environment may not seem a useful medium for dehydration reactions, such as that of **6** as observed here at 250 and 290 °C (entries 10 and 11, Table 1), dehydrations in high-temperature water are well recognized, the conversion of cyclohexanol to cyclohexene having been recently investigated.⁸

In the elimination of water from **6**, the unexpected preferential formation of **2** instead of **5** raised an intriguing mechanistic issue. Unlike in **5**, the side-chain double bond of **2** was not in conjugation with the aromatic ring and was monosubstituted rather than disubstituted. The 8:1 ratio of **2**:**5** that was produced at 250 °C

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suggested either that expulsion of water may not have occurred from **6** primarily *via* a Saytzeff-type process by which the more substituted, fully conjugated olefin **5** would have been expected¹⁹ or that **2** may have predominated as a result of allylic strain implicating the aryl hydroxyl group.²⁰ The unusual selectivity did not extend to the behavior of 1-phenyl-2-propanol, however. In water at 250 °C for 1 h, this phenyl-2-propanol underwent only 5% conversion, but gave a mixture of *cis* and *trans*-phenylpropenes that accorded with the Saytzeff rule. Heating in dilute H₂SO₄ also afforded the 1-phenylprop-2-enes primarily, but in higher conversion. These results thus rendered the second suggestion more likely.

The accumulation of dihydrobenzofuran **7** at higher temperature, its formation from **1**, **2**, **5**, or **6**, and its relative lack of reactivity at 290 °C all indicated that of the C₉ compounds, **7** was the most thermodynamically stable product. Even in dilute H₂SO₄, ring opening of **7** occurred to only a minor extent (entry 13, Table 1). Nonetheless, this highlighted the complexity of the equilibria involved, and confirmed that slight adjustments to the reaction conditions could lead to significantly different (but reproducible) outcomes.

The pathway proposed in Scheme 1 appears to satisfy data in Figure 1, Table 1, and the above discussion. However, owing to the interrelationship among phenols **2**, **4**, **5**, and to some extent **6**, it was difficult to establish which of these alcohols could give dihydrofuran **7** directly.

The influence of water on the course of reaction was next assessed. In a control experiment, neat allyl phenyl ether (**1**) was heated in the autoclave for 1 h at 290 °C (entry 3, Table 1). Allylphenol **2** was formed in high conversion, with only small amounts of **3**, **4**, **5**, and **7** detected. This result indicated that in the absence of water the phenolic product **2** could not readily promote autocatalytic reactions such as ring closure to **7** or isomerization to **5**. The product distribution contrasted markedly with that obtained after **1** was heated at lower temperatures in water for the same time to afford products in common with those reported in TFA at 60 °C (see Figure 1, Table 1, and discussion above). This showed that water behaved primarily as a medium for Claisen rearrangement at about 200 °C but indicated that at higher temperature it also played catalytic and participatory roles.

In the MBR and autoclave reactions of **1** in water, the (unbuffered) aqueous phase had a pH ranging between 3.5 and 4.5 after completion of heating, cooling, and extraction of the products. Initially, this acidity was attributed to the presence of small amounts of unextracted phenolic products. Significantly though, after the phenolics **2**, **5**, and **6** were heated individually (see Table 1) and the products were extracted, the pH of the aqueous phase was higher, in the range 4.8–5.4. The consequences of these differences in pH were investigated by heating **2** in dilute sulfuric acid at 290 °C (entry 7, Table 1). After extraction, the pH of the aqueous phase was 3.8. In sharp contrast with reactions of **2** at 290 °C in unacidified water (entry 6 Table 1), only 5% of the starting material was recovered. Major products were

dihydrobenzofuran **7** (64%), **3** (5%), **4** (6%), and **5** (20%), a product distribution comparable with that obtained from **1** in water at 240–250 °C (Figure 1). These results were consistent with recent findings that addition of traces of acid can substantially enhance the rates of reactions in high-temperature water.⁸

Comparison of Autoclave and MBR Reactions of 1. Many publications on microwave-assisted organic chemistry have referred to accelerated reactions, and workers have speculated about the role of microwaves. However, suggestions of specific activation at a controlled temperature in homogeneous media now have been rejected.²¹ Complex reactions may be more difficult to explore in this regard though, and enhanced rates of catalytic transfer hydrogenation were recently attributed to microwave-assistance in transport processes at the catalyst and liquid interfaces in a multiphase system.²²

In the present work, the main differences between the sets of results from the MBR and autoclave concerned the relative rates of diminution of **1**; temperatures at which maximal conversion to specific products occurred; the extent of conversion to some of these products; and the relative rates of formation of **7**.

To elaborate, 95% conversion of ether **1** was achieved at 230 °C in the MBR, but nearly 20 °C higher in the autoclave. The greatest concentration of allylphenol **2** was obtained at 200 °C in the MBR, but 15 °C higher in the autoclave; hydroxyphenol **6** at 225 °C (MBR) and 245 °C (autoclave); and ether **7** at 250 °C (MBR) and 275 °C (autoclave). The highest conversions observed for **2** were 56% (MBR) and 67% (autoclave); hydroxyphenol **6**, 37% (both methods); ether **7**, 72% (MBR) and 66% (autoclave); isopropenylphenols **4** and **5**, 12% (MBR) and 23% (autoclave); and phenol (**3**), 9% (MBR) and 5% (autoclave). From 230 to 250 °C conversion to **7** increased at the rate of 2%/°C with the MBR, but only at 1.3%/°C in the autoclave.

These results indicate that in aspects other than the greatest extent of conversion of **1** to 2-allylphenol (**2**), and to the mixture of propenylphenols **4** and **5**, microwave heating afforded higher conversions. However, rearrangement of **1** in water was already known to proceed in 84% conversion at 240 °C within only 10 min.¹ So the present work has shown that if aqueous conditions are to be employed for preparative conversion of **1** to products such as **2**, the optimal heating time may not be 1 h.

With conductive heating by conventional autoclave, thermal gradients develop, and despite stirring, only part of the sample is at the temperature of the applied heat. Accordingly, in this work the measured temperature was dependent upon the positioning of thermal sensors. In calibrations of the vessel, differences of ±7 °C were observed within the sample.

On the other hand, with the MBR the microwave energy was primarily absorbed by the sample directly, and since the vessel was fabricated from polytetrafluoroethylene (PTFE), conductive heat losses were minimal. Further, owing to bulk heating by microwaves, the whole of the sample could be irradiated simultaneously. These factors, combined with efficient stirring, virtually eliminate temperature gradients. The differences between the nature and properties of conventional and

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microwave heating probably account for the variability between the data obtained with the autoclave and the MBR. In support of this conclusion, Mingos²³ has estimated that rate enhancements of 100–1000-fold would be required before specific microwave effects could be invoked.

Advantages offered by microwave-assistance for synthesis include capabilities for rapid heating and cooling, control of heating, concurrent heating and cooling, differential heating, and ease of use for high-temperature reactions.^{1–3} Not all of these benefits are attainable through conventional heating techniques. However, since pressurized microwave equipment is not yet widely available for organic synthesis, it may be necessary to adapt microwave-assisted reactions for autoclaves. These findings indicate that if the microwave conditions can be adequately mimicked (a proviso that may not always hold), conventional heating will produce a comparable outcome.

Conclusion

This work has shown that temperatures available for useful synthetic reactions in water can be at least as high as 290 °C. However, optimal conditions for a given transformation can occur within a narrow range of time and temperature. Although the convenience of high-temperature water as a solvent and/or medium for preparative organic chemistry has been demonstrated, potential opportunities will only be fully realized through high conversions and yields for a diverse range of reactions, as well as the introduction of environmentally benign isolation techniques. Our work is progressing on these fronts.

Experimental Section

General Methods. ¹H and ¹³C NMR, EIMS, and GC analyses were carried out as previously described.²⁴ Authentic compounds **1**, **2**, **3**, and the mixture of *cis* and *trans*-2-(prop-

1-enyl)phenols (**4** and **5**) were commercially available. Products **6** and **7** were isolated from reaction mixtures (see below) and used for reactions in Table 1. Quantitative data presented in Table 1 and Figure 1 were derived predominantly from ¹H NMR spectra and were in close agreement with those obtained by GCMS analysis.

2-(2-Hydroxypropyl)phenol (6). Allylphenyl ether (**1**; 3.3 g) was injected under a pressure of argon into water (95 mL) preheated to 275 °C in the autoclave. The temperature was maintained at 275 °C for 10 min with stirring, and then the reactor was cooled and the organics extracted with Et₂O (3 × 100 mL). GC analysis indicated that conversion of **1** to **6** was 30%. The combined organic phases were dried (MgSO₄) and the solvent was removed. A portion of the residue (1.0 g) was subjected to flash chromatography on silica gel, with EtOAc/cyclohexane 3:7 as eluent, to afford pure **6** (0.3 g): ¹H NMR (CDCl₃) δ 1.20 (d, 3H, *J* = 6.3 Hz), 2.70–2.95 (m, 2H), 4.05–4.13 (m, 1H), 5.8–6.2 (bs, 2H), 6.8–7.2 (m, 4H), in agreement with literature values;²⁵ ¹³C NMR (CDCl₃) δ 22.9, 40.6, 69.9, 116.8, 120.5, 125.5, 128.3, 131.8, 155.0; MS (EI) *m/z* (relative intensity) 152 (M⁺, 23), 108 (100), 107 (62).

2-Methyl-2,3-dihydrobenzofuran (7). Allylphenyl ether (**1**; 1.85 g) was injected under a pressure of argon into water (50 mL) at 290 °C. The system was maintained at this temperature with stirring for 2 h and then cooled. The resultant mixture was extracted with Et₂O (3 × 50 mL), and the combined organic phases were dried (MgSO₄) and concentrated to afford an oil (1.4 g) that, by GC analysis contained mainly **7** (64%). The oil was extracted with 1 M NaOH and purified by flash chromatography on silica gel, using CH₂Cl₂ as eluent to afford **7** (0.6 g; 32%). ¹H NMR (CDCl₃) δ 1.40 (d, 3H, *J* = 6 Hz), 2.65–3.30 (m, 2H), 4.75–4.95 (m, 1H), 6.6–7.1 (m, 4H), in accordance with literature values;²⁶ MS (EI) 134 (M⁺, 100), 133 (44), 119 (64), 115 (29), 91 (84).

Example Reaction under Microwave Heating. A mixture of allyl phenyl ether (**1**; 2 g) in water (50 mL) was placed in the microwave reaction vessel. The vessel contents were purged with argon, and then the stirred contents were rapidly heated by the application of microwave power to 230 °C, held at this temperature for 1 h, and rapidly cooled with the cold finger facility to ambient temperature. The resultant mixture was then extracted with diethyl ether (3 × 25 mL), and the combined organic phase was dried (MgSO₄) and concentrated to give the product mixture as a brown oil (1.8 g). The products were analyzed by GC, EIMS, and ¹H NMR.

JO961095J

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