of the Grignard reagent to the organometallic precursor of **11**.

Only a small amount of **11** was found in a reaction in which **10** and allylmagnesium chloride were refluxed in THF for 24 h.

(b) With Allylmagnesium Chloride and 1-Phenyl-1-propene. As in the reaction of **10** described above, THF (8.6 mL) was distilled from a commercial THF solution (15.5 mL, 3.0 M, 46.5 mmol) of allylmagnesium chloride. The solution was cooled, and a solution of **10** (2.50 g, 15.5 mmol), 1-phenyl-1-propene (1.83 g, 15.5 mmol), and dodecane (2.64 g, 15.5 mmol) in toluene (40 mL) was added. After the addition, heating was resumed and distillation continued until a head temperature of 70 °C was reached (1.8 mL of distillate was collected). The reaction mixture that remained was refluxed for 24 h and then worked up by using procedure B. After removal of most of the solvent by distillation, distillation at reduced pressure gave a liquid: 5.2 g; bp 40-90 °C (7 torr). Its ^{1}H NMR spectrum had absorptions due to 1-phenyl-1-propene, **11**, and dodecane but only faint absorptions due to **10**. GC analysis (column B) showed four major peaks, corresponding to 1-phenyl-1-propene, **10** (retention time 2.7 relative to 1-phenyl-1-propene), dodecane ($t_R = 3.5$), and **11** ($t_R = 18.9$). Presumably, no product of addition to 1-phenyl-1-propene was present, since no unidentified peaks with retention times greater than that of 1-phenyl-1-propene were noted. From the GC analysis, the amounts of **10** and **11** corresponded respectively to 12% and 53% of the **10** used initially.

(c) With Butylmagnesium Bromide. No evidence for an addition product was obtained and the reactant was isolated in good yield from a reaction in which **10** and butylmagnesium bromide in methylcyclohexane (the Grignard reagent solution was prepared by using a procedure already described)[43] were refluxed for 8 h.

Reactions of 3-(Dimethylamino)-1-phenyl-1-propyne (12). (a) With Allylmagnesium Chloride; Isolation of 13. A solution of **12** (2.00 g, 12.6 mmol) in THF (25 mL) was added to a commercial THF solution of allylmagnesium chloride (12.5 mL, 3.0 M, 37.5 mmol). The resulting solution was refluxed for 20 h and then worked up by using procedure A. The solvent was removed at reduced pressure and the remainder distilled to give **13**: 1.24 g (6.2 mmol, 49%); bp 94-96 °C (1 torr); IR (CCl_4) 1635 cm^{-1} (C=C); ^{1}H NMR (CCl_4) δ 2.19 (s, 6, CH_3), 2.88 (br s, 2, CH_2N), 3.04 (br d, 2, J = 6 Hz, CH_2CH=), 4.91 (m, 1, =CHH), 5.13 (m, 1, =CHH), 5.33-6.31 (m, 1, =$CHCH_2$), 6.50 (br s, 1, =CHPh), 7.20 (m, 5, Ph). Anal. Calcd for $C_{14}H_{19}N$: C, 83.53; H, 9.51; N, 6.96. Found: C, 83.77; H, 9.77; N, 6.85.

(b) With Allylmagnesium Chloride and 1-Phenyl-1-butyne. A solution of **12** (1.00 g, 6.3 mmol) and 1-phenyl-1-butyne (0.82 g, 6.3 mmol) in THF (25 mL) was added slowly to a commercial THF solution of allylmagnesium chloride (6.3 mL, 3.0 M, 18.9 mmol). The resulting solution was refluxed for 15 h and then worked up by using procedure A. The solvent was removed at reduced pressure. GC analysis (Column C, 185 °C) of the liquid remaining after removal of the solvent at reduced pressure showed peaks due to an unidentified component (4% of the total peak area), 1-phenyl-1-butyne (retention time 1.9 relative to unidentified component), **12** ($t_R = 4.5$), and **19** ($t_R = 5.3$). Yields of 1-phenyl-1-butyne (67%), **12** (20%), and **13** (16%) were determined by using a dodecane standard. Presumably, no product of addition to 1-phenyl-1-butyne was present since no unidentified peak with retention time greater than that of 1-phenyl-1-butyne was noted.

Acknowledgment. We are grateful to the National Science Foundation for support of this research and for aiding in the purchase of the NMR spectrometers and the mass spectrometer that were used. We thank Dr. Robert D. Minard for obtaining the mass spectra.

Registry No. **1**, 589-09-3; **2**, 78168-73-7; **3**, 62-53-3; **5b**, 4049-81-4; **6**, 4360-51-4; **7**, 17214-47-0; **8**, 78168-74-8; **9**, 536-74-3; **10**, 33962-90-2; **11**, 32529-06-9; **12**, 2568-65-2; **13**, 32529-07-0; allyl chloride, 107-05-1; butyl bromide, 109-65-9; 2-methyl-2-propenyl chloride, 563-47-3; 2,5-dimethyl-1,5-hexadiene, 627-58-7; allyl phenyl ether, 1746-13-0; phenol, 108-95-2; allylamine, 107-11-9; *N*-allyl-*p*-toluenesulfonamide, 50487-71-3; 2-methyl-4-penten-1-ol, 5673-98-3; 6-hepten-1-ol, 4117-10-6; diallylamine, 124-02-7; 1-phenyl-1-propene, 637-50-3; *N*-allyl-*N*-methylaniline, 4383-22-6; *N*,*N*-dimethylallylamine, 2155-94-4; *N*,*N*-diethylallylamine, 5666-17-1; 1-phenyl-1-butyne, 622-76-4.

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[43] Bryce-Smith, D.; Blues, E. T. *Org. Synth.* **1967**, *47*, 113.

Additions of Allylic Grignard Reagents to *o*-Allylphenol

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Reactions of *o*-allylphenol (**1a**) with allylmagnesium chloride or bromide furnished 6-(*o*-hydroxyphenyl)-1-hexene (**2a**) and 4-methyl-5-(*o*-hydroxyphenyl)-1-pentene (**3a**), products resulting from both possible orientations of addition. A reaction of **1a** and (2-methyl-2-propenyl)magnesium chloride gave only 6-(*o*-hydroxyphenyl)-2-methyl-1-hexene (**2b**). From comparisons with reactions of allylmagnesium chloride with *o*-allylanisole and allylbenzene, it is concluded that the metalated phenolic hydroxyl group, even though relatively remote from the double bond, assists the additions to **1a**.

Addition of an excess of an organomagnesium compound, particularly if allylic, to the multiple bond of an alkenol, alkynol, or allenol is often assisted by the metalated hydroxyl group.[1] Metalated amino groups also assist addition, but some comparisons suggest that their assistance is less effective than that afforded by metalated hydroxyl groups.[2,3] Moreover, one comparison suggests that a phenylamino group is more effective than a primary amino group.[3] These conclusions are consistent with a proposal that effectiveness in assisting additions may increase with decreasing basicity of the metalated assisting group. If this proposal is correct, than the metalated hydroxyl group of a phenol might be even more effective than that of an alcohol. In the work described in this paper, we studied reactions of allylic Grignard reagents with *o*-allylphenol (**1a**).

Results and Discussion

No new compounds were obtained from reactions of *o*-allylphenol (**1a**, eq 1) and an excess of allylmagnesium

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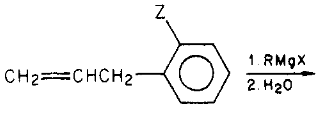
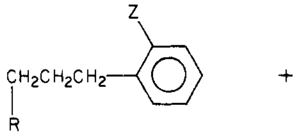
[1] See ref 3 for a list of relevant references.

[2] Eisch, J. J.; Merkley, J. H. *J. Am. Chem. Soc.* **1979**, *101*, 1148.

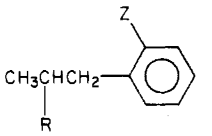
[3] Richey, H. G., Jr.; Moses, L. M.; Domalski, M. S.; Erickson, W. F.; Heyn, A. S. *J. Org. Chem.*, previous paper in this issue.



1a, Z = HO
c, Z = CH_3O
d, Z = H



2a, Z = HO; R = $CH_2{=}CHCH_2$
b, X = HO; R = $CH_2{=}CH(CH_3)CH_2$
c, Z = CH_3O; R = $CH_2{=}CHCH_2$
d, Z = H; R = $CH_2{=}CHCH_2$



(1)

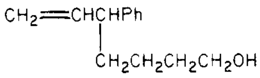
3a, Z = HO; R = $CH_2{=}CHCH_2$
b, X = HO; R = $CH_2{=}CH(CH_3)CH_2$
c, Z = CH_3O; R = $CH_2{=}CHCH_2$
d, Z = H; R = $CH_2{=}CHCH_2$

chloride in refluxing diethyl ether or tetrahydrofuran (THF) solutions. However, GC analysis[4] after 3 h of a reaction at 100 °C in diethyl ether showed the presence of 58% of **2a** and 29% of **3a**, products resulting from both possible orientations of addition. Analysis after 36 h of a qualitatively somewhat slower reaction at 100 °C in THF indicated the presence of 62% of **2a** and 28% of **3a**. A similar reaction at 100 °C in THF of **1a** and allylmagnesium bromide gave 70% of **2a** and 16% of **3a** after 61 h.

GC analysis of a reaction of **1a** and (2-methyl-2-propenyl)magnesium chloride in THF at 100 °C indicated the formation of 84% of **2b**.[4] No more than 2% of another addition product could have been present. The greater tendency of 2-methyl-2-propenyl than of allyl to become attached to the terminal carbon of the alkene may be the result of some steric effect of the methyl group. However, if such a factor is present, it must not drastically affect the rate of addition, which qualitatively was at least as fast for the 2-methyl-2-propenyl as for the allyl Grignard reagent.[5]

Even though additions to **1a** were slow, requiring 100 °C rather than reflux temperatures to achieve practical rates, they were considerably faster than adddditions to either *o*-allylanisole (**1c**) or allylbenzene (**1d**). In a reaction of *o*-allylanisole (**1c**) and allylmagnesium chloride at 100 °C in THF, only 4.5% of **3c** was present, and 86% of **1c** remained after 60 h. Following this time, the amount of **3c** did not increase, perhaps because by then the Grignard reagent had reacted in other ways.

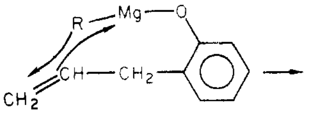
Addition product **3d** formed slowly in a reaction of allylbenzene (**1d**) with allylmagnesium chloride at 100 °C in diethyl ether. GC analysis showed the yield of **3d** to reach 13% after 44 h, following which time it did not increase further. The only other new compound detected in significant amounts did not contain an aromatic ring (see Experimental Section). GC analysis[4] of a reaction of **1d** and allylmagnesium chloride at 100 °C in THF showed the appearance of three minor peaks. One was shown to be due to **4**, which presumably arose from attack of metalated **1d** on the solvent. This compound has also been isolated from a reaction in THF of cinnamyl bromide, triphenyltin chloride, and an excess of magnesium.[6] The identities of the compounds responsible for the other two peaks were not established (see Experimental Section). However, **2d** could not have been present in significant amounts.



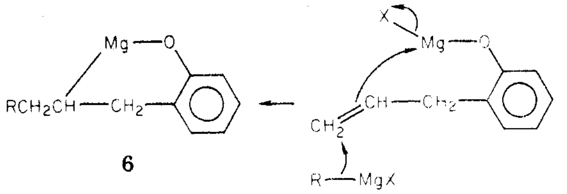
$$CH_2{=}CHCHPh(CH_2CH_2CH_2CH_2OH)$$

4

Since additions to **1a** are qualitatively faster than to either **1c** or **1d**, we believe that the metalated hydroxyl group of **1a** assists the additions. Moreover, the observation that the orientation of addition to **1a** is different than that to **1c** and **1d** also suggests that something different is involved in the reactions with **1a**. The products of addition of allylmagnesium chloride to **1c** and **1d** are those of attachment of allyl to the nonterminal carbon. Such attachment has also been observed in additions of allylic Grignard reagents to terminal alkenes lacking other functional groups.[7] By contrast, in the additions to **1a**, only terminal attachment was observed with (2-methyl-2-propenyl)magnesium chloride and predominant terminal attachment with allyl Grignard reagents. Such attachment would be consistent with either an intramolecular transformation such as **5** → **6**[8] (eq 2) or an intermolecular process such as **7** → **6**,[9] proposals that have been made for the manner in which the metalated hydroxyl group assists addition.



5



6

7

(2)

We conclude that the metalated, phenolic hydroxyl group of **1a** is remarkably effective in assisting additions. We cannot compare its effectiveness with that of the

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(4) See the Experimental Section of ref 3 for a description of the procedure and assumption used in determining yields by GC analysis.

(5) Addition of (2-methyl-2-propenyl)magnesium bromide to bicyclo[2.2.1]hept-2-ene is somewhat faster than addition of allylmagnesium bromide: Lehmkuhl, H.; Janssen, E. *Justus Liebigs Ann. Chem.* **1978**, 1854.

(6) Tanigawa, Y.; Moritani, I.; Nishida, S. *J. Organomet. Chem.* **1971**, *28*, 73.

(7) Lehmkuhl, H.; Reinehr, D.; Schomburg, G.; Henneberg, D.; Damen, H.; Schroth, G. *Justus Liebigs Ann. Chem.* **1975**, 103. Lehmkuhl, H.; Reinehr, D.; Henneberg, D.; Schomburg, G.; Schroth, G. *Ibid.* **1975**, 119. Lehmkuhl, H.; Bergstein, W.; Henneberg, D.; Janssen, E.; Olbrysch, O.; Reinehr, D.; Schomburg, G. *Ibid.* **1975**, 1176.

(8) Eisch, J. J.; Husk, G. R. *J. Am. Chem. Soc.* **1965**, *87*, 4194.

(9) Chêrest, M.; Felkin, H.; Frajerman, C.; Lion, C.; Roussi, G.; Swierczewski, G. *Tetrahedron Lett.* **1966**, 875.

metalated hydroxyl group of an alcohol. As far as we know, there are no studies of reactions of Grignard reagents with alcohols containing δ,ϵ-alkene functions (let alone with ones in which, as in **1a**, C_α–C_β maintains a cisoid relationship between OH and C_γ). However, addition of an allyl Grignard reagent was not observed even to an alkenol with a γ,δ-alkene function.[2]

No evidence for a significant amount of an addition product was found in reactions of **1a** and butyllithium in hexane in the presence of *N,N,N′,N′*-tetramethylethylenediamine at ambient temperature, at reflux temperature, or at 100 °C.

Experimental Section

The general experimental information and the procedures for reactions with Grignard reagents are identical with those described in the accompanying paper.[3] GC column E was used. The contents of ampules heated at 100 °C generally appeared to be homogeneous.

Materials. (a) Substrates for Reactions with Organometallic Compounds. *o*-Allylphenol (**1a**) was prepared from allyl phenyl ether as previously reported:[10] bp 53 °C (0.10 torr) [lit.[10] bp 109–110 °C (22 torr)]. *o*-Allylanisole (**1c**) was prepared from **1a** as previously reported:[11] bp 50 °C (0.10 torr) [lit.[11] bp 101–102 °C (22 torr)]. Allylbenzene (**1d**), a commercial sample (Aldrich Chemical Co.), was distilled at reduced pressure before use.

(b) Other Compounds. Except as noted, these were as described in the accompanying paper.[3] Butyllithium in hexane was a commercial sample (Ventron Corp). Hexane was stored over molecular sieves (4A). *N,N,N′,N′*-Tetramethylethylenediamine (TMEDA, Aldrich Chemical Co.) was distilled at reduced pressure prior to use. Allyl bromide (Aldrich Chemical Co.) was distilled and then stored over molecular sieves (4A).

Reactions of *o*-Allylphenol (1a). (a) With Allylmagnesium Chloride in Diethyl Ether. A solution of **1a** (3.92 g, 29 mmol) in diethyl ether (25 mL) was added to a Grignard reagent solution prepared from allyl chloride (9.24 g, 121 mmol) and magnesium (3.06 g, 126 mmol) in diethyl ether (70 mL). The resulting suspension was stirred vigorously to ensure that the suspended solid was distributed reasonably uniformly, and the mixture was sealed in ampules which were then heated at 100°. GC analysis (200 °C) after hydrolysis showed the presence of three major peaks that, as described below, were shown to be due to **1a**, **3a**, and **2a** (retention times relative to tridecane of 0.77 for **1a**, 1.97 for **3a**, and 2.37 for **2a**). The following compositions were observed: 1 h, 16% **1a**, 28% **3a**, and 45% **2a**; 2 h, 2%, 28%, and 57%; 3 h, 0%, 29%, and 58%; 27 h, 0%, 30%, and 58%. Distillation of the material representing about 75% of the original reaction solution gave three fractions. GC analysis of fraction one [0.80 g; bp 70–75 °C (0.40 torr)] showed it to contain 5% of **1a**, 26% of **2a**, and 69% of **3a**. Fraction two [1.00 g; bp 76–80 °C (0.40 torr)] contained 55% of **2a** and 45% of **3a**, and fraction three [0.46 g; bp 84 °C (0.45 torr)] contained 68% of **2a** and 32% of **3a**.

The compound responsible for the first GC peak was shown to be **1a** by comparing its IR and ^{1}H NMR spectra with those of an authentic sample.

The compound responsible for the second peak was shown to be **3a** (total amount in the distillation fractions was 1.15 g, 6.53 mmol, 30% yield): IR (CCl_4) 3586 (OH), 1636 ($C{=}C$) cm^{-1}; ^{1}H NMR (CCl_4) δ 0.84 (d, 3, *J* = 6 Hz, CH_3), 1.73–2.18 (c, 3, $C\mathbf{H}C\mathbf{H}_2CH{=}$), 2.28–2.74 (m, 2, CH_2Ar), 4.86 (s, 1, OH), 4.68–5.13 (c, 2, $={CH_2}$), 5.33–5.98 (m, 1, $={CH}$), 6.34–7.04 (c, 4, aryl H's); low-resolution mass spectrum, *m/z* (relative intensity) 176 (14), 175 (91), 160 (9), 133 (11), 132 (13), 119 (3), 118 (6), 117 (4), 107 (57), 106 (100), 105 (11), 104 (14), 93 (23), 77 (71); high-resolution mass spectrum, *m/z* 176.1208 (M^+, calcd for $C_{12}H_{16}O$ 176.1200).

The compound responsible for the third GC peak was shown to be **2a** (total amount in the distillation fractions was 1.07 g, 6.08 mmol, 28% yield): IR (CCl_4) 3590 (OH), 1633 ($C{=}C$) cm^{-1}; ^{1}H NMR (CCl_4) δ 1.35–1.73 (c, 4, $CH_2C\mathbf{H}_2C\mathbf{H}_2CH_2$), 1.86–2.27 (m, 2, $C\mathbf{H}_2CH{=}$), 2.43–2.75 (m, 2, CH_2Ar), 5.02 (s, 1, OH), 4.73–5.27 (c, 2, $={CH_2}$), 5.43–6.14 (m, 1, $={CH}$), 6.44–7.21 (c, 4, aryl H's); low-resolution mass spectrum, *m/z* (relative intensity) 176 (22), 132 (14), 119 (28), 118 (33), 107 (100); high-resolution mass spectrum, *m/z* 176.1222 (M^+, calcd for $C_{12}H_{16}O$ 176.1200).

GC analysis of aliquots of a similar reaction in refluxing diethyl ether showed **1a** to be the only significant component, even after 72 h.

(b) With Allylmagnesium Chloride in THF. A solution of **1a** (3.83 g, 28 mmol) in THF (20 mL) was added to a Grignard reagent solution prepared from allyl chloride (15.3 g, 200 mmol) and magnesium (4.80 g, 197 mmol) in THF (65 mL). The resulting solution was sealed in ampules which were then heated at 100 °C. GC analysis indicated three components which were shown by their retention times and IR and ^{1}H NMR spectra to be **1a**, **2a**, and **3a**. The following compositions were observed: 1 h, 83% **1a**, 7% **2a**, and 2% **3a**; 3 h, 61%, 25%, and 5%; 5 h, 50%, 33%, and 8%; 8 h, 38%, 44%, and 9%; 12 h, 18%, 54%, and 10%; 25 h, <1%, 62%, and 27%; 36 h, 0%, 62%, and 28%; 46 h, 0%, 62%, and 28%. Distillation of the material representing about 80% of the original reaction solution gave three fractions. GC analysis of fraction 1 [0.36 g; bp 35–37.5 °C (0.10 torr)] showed it to be mainly **1a**. GC analysis showed fraction 2 [1.52 g; bp 71–76.5 °C (0.15 torr)] to be 10% **1a**, 53% **2a**, and 37% **3a** and fraction 3 [0.18 g; bp 93.5–106 °C (0.15 torr)] to be 74% **2a** and 26% **3a**. The yield of **2a** (total amount in the distillation fractions was 0.61 g, 3.46 mmol) was 15%, and that of **3a** (0.94 g, 5.34 mmol) was 23%.

GC analysis of aliquots of a similar reaction in refluxing THF showed **1a** to be the only significant component, even after 72 h. Workup and distillation gave a liquid that was shown by its IR and ^{1}H NMR spectra to be essentially pure **1a**.

(c) With Allylmagnesium Bromide in THF. A reaction mixture similar to that described immediately above except for being prepared with allylmagnesium bromide was sealed into ampules which then were heated at 100 °C. The somewhat erratic compositions determined by GC analysis included the following: 14 h, 59% **1a**, 29% **2a**, and 3% **3a**; 24 h, 18%, 61%, and 8%; 38 h, 14%, 62%, and 10%; 50 h, 7%, 68%, and 16%; 61 h, 4%, 70%, and 16%.

Reaction of *o*-Allylphenol (1a) with (2-Methyl-2-propenyl)magnesium Chloride. A solution of **1a** (1.27 g, 9.9 mmol) in THF (15 mL) was added to a Grignard reagent solution prepared from 3-chloro-2-methyl-1-propene (7.45 g, 82 mmol) and magnesium (2.00 g, 82 mmol) in THF (50 mL). The reaction mixture was sealed in ampules which then were heated at 100 °C. GC analysis (214 °C) showed the presence of two major peaks that were due to **1a** and **2b** (retention times relative to tridecane of 0.75 for **1a** and 3.24 for **2b**). The following compositions were observed: 1 h, 50% **1a** and 34% **2b**; 3 h, 34% and 50%; 4.5 h, 21% and 61%; 7.5 h, 10% and 76%; 16 h, 6% and 82%; 24 h, 6% and 83%; 41 h, 6% and 84%. Distillation of the organic material representing about 80% of the original reaction mixture gave two fractions. GC analysis showed fraction 1 [0.15 g; bp 47–49 °C (0.10 torr)] to be almost completely **1a**. Fraction 2 [0.50 g; bp 78–90 °C (0.40 torr)] was about 11% **1a** and 84% **2b**; three small peaks, due to unidentified components, fell between the peaks due to **1a** and **2b** and totaled about 5% of the peak area.

The compound responsible for the second major GC peak was shown to be **2b**: 0.42 g (2.21 mmol, 29% yield); IR (CCl_4) 3596 (OH), 1646 ($C{=}C$) cm^{-1}; ^{1}H NMR (CCl_4) δ 1.35–1.78 (c, 4, $C\mathbf{H}_2C\mathbf{H}_2CH_2Ar$), 1.68 (s, 3, CH_3), 1.88–2.23 (m, 2, $CH_2C{=}$), 2.40–2.83 (m, 2, CH_2Ar), 4.64 (s, 1, OH), 4.53–4.93 (c, 2, $={CH_2}$), 6.47–7.18 (m, 4, aryl H's); low-resolution mass spectrum, *m/z* (relative intensity) 190 (44), 134 (22), 133 (17), 121 (11), 120 (56), 119 (6), 108 (22), 107 (100), 91 (17), 83 (22), 80 (11), 77 (33), 55 (22); high-resolution mass spectrum, *m/z* 190.1357 (M^+, calcd for $C_{13}H_{18}O$ 190.1357).

Reaction of *o*-Allylanisole (1c) with Allylmagnesium Chloride. A solution of **1c** (2.48 g, 17 mmol) in THF (20 mL) was added to a Grignard reagent solution prepared from allyl chloride (9.73 g, 127 mmol) and magnesium (2.99 g, 123 mmol) in THF (55 mL). The resulting solution was sealed in ampules which were then heated at 100 °C. GC analysis (187 °C) showed the presence of two peaks that were due to **1c** and **3c** (retention times relative to tridecane of 0.59 for **1c** and 1.47 for **3c**). The following yields were observed: 48 h, 90% **1c** and 2.5% **3c**; 60

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(10) Jacobs, W. A.; Heidelberger, M. *J. Am. Chem. Soc.* **1917**, *39*, 2188.
(11) Adams, R.; Rindfusz, R. E. *J. Am. Chem. Soc.* **1919**, *41*, 648.

h and longer times, 86% **1c** and 4.5% **3c**. Distillation of the organic material representing about 80% of the original reaction solution gave two fractions. GC analysis of fraction 1 [1.30 g; bp 31–50 °C (0.10 torr)] showed it to be principally **1c**. Fraction 2 [0.37 g; bp 60–80 °C (0.10 torr)] was 85% **1c** and 15% **3c**.

The compound responsible for the second peak was shown to be **3c**: 0.06 g (0.32 mmol, 2% yield); IR (CCl_4) 1635 cm^{-1} (C=C); ^{1}H NMR (CCl_4) δ 0.86 (d, 2, J = 6 Hz, $CHCH_3$), 1.80–2.20 (c, 3, $CHCH_2CH$=), 2.35–2.67 (m, 2, CH_2Ar), 3.78 (s, 3, OCH_3), 4.74–5.14 (c, 2, =CH_2), 5.33–6.05 (m, 1, =CH), 6.74–7.15 (c, 4, aryl H's); low-resolution mass spectrum, m/z (relative intensity) 190 (14), 149 (11), 148 (28), 122 (21), 121 (100), 91 (64); high-resolution mass spectrum, m/z 190.1347 (M$^+$, calcd for $C_{13}H_{18}O$ 190.1357).

Reactions of Allylbenzene (1d) with Allylmagnesium Chloride. (a) In Diethyl Ether. A solution of **1d** (2.02 g, 17 mmol) in diethyl ether (20 mL) was added to a Grignard reagent solution prepared from allyl chloride (9.35 g, 122 mmol) and magnesium (3.01 g, 124 mmol) in diethyl ether (65 mL). The resulting solution was sealed in ampules which were then heated at 100 °C. GC analysis (183 °C) showed three peaks. The first and third were shown to be due to **1d** and **3d**, and the second was probably due to 1-allyl-3-methylcyclopentane (retention times relative to tridecane of 0.29 for **1d**, 0.58 for the second component, and 0.73 for **3d**). The yields after 44 h were 74% of **1d**, 7% of the second component (assuming it to have the molecular weight of 1-allyl-3-methylcyclopentane), and 13% of **3d**, and did not change after that time. A similar reaction gave essentially the same results. Distillation of the organic material representing about 60% of the original reaction solution gave a fraction [0.51 g; bp 45–60 °C (0.20 torr)] shown by GC analysis to be 12% **1d**, 30% of the second component, and 57% **3d**.

The compound responsible for the second peak is thought to be 1-allyl-3-methylcyclopentane. This compound is known to result from the reaction of allylmagnesium chloride and 1,5-hexadiene (a byproduct of formation of the allyl Grignard reagent).[12] The IR spectrum of collected material showed an absorption (C=C) at 1640 cm^{-1}; the weak ^{1}H NMR spectrum (CCl_4) showed only a little aryl H absorption and resembled that already reported[12] for this compound: δ 0.98 (d, J = 6 Hz, CH_3), 1.15–1.51 (c), 1.55–2.15 (c), 4.48–5.20 (c, =CH_2), 5.40–6.23 (=CH).

The compound responsible for the third peak was shown to be **3d**: 0.29 g (1.81 mmol, 18% yield); IR (CCl_4) 1639 cm^{-1} (C=C); ^{1}H NMR (CCl_4) δ 0.86 (d, 3, J = 6 Hz, CH_3), 1.67–2.30 (c, 3, $CHCH_2CH$=), 2.34–2.68 (m, 2, CH_2Ar), 4.74–5.23 (c, 2, =CH_2), 5.44–6.18 (m, 1, =CH), 6.98–7.35 (br s in appearance, 5, aryl H's); low-resolution mass spectrum, m/z (relative intensity) 160 (5), 118 (14), 117 (53), 116 (7), 104 (5), 92 (32), 91 (100), 77 (4), 68 (21), 64 (9), 41 (30); high-resolution mass spectrum, m/z 160.1258 (M$^+$, calcd for $C_{12}H_{16}$ 160.1251).

(b) In THF. A solution of **1d** (2.46 g, 21 mmol) in THF (25 mL) was added to a Grignard reagent solution prepared from allyl chloride (11.1 g, 145 mmol) and magnesium (3.46 g, 142 mmol) in THF (55 mL). The resulting reaction mixture was sealed in ampules which were then heated at 100 °C. GC analysis (227 °C) showed four peaks. The first was shown to be due to **1d** and the fourth to **4** (retention times relative to heptadecane of 0.105 for **1d**, 0.21 and 0.26 for the second and third components, and 0.71 for **4**). After 90 h, the composition (percent of total area) was 70% **1d**, 22% component two, 8% component three, and 0% **4**, and after 9 days it was 65%, 20%, 7%, and 8%, respectively.

In a similar experiment, about 95% of a similar solution was heated for 11 days in ampules. Distillation gave two fractions. GC analysis showed fraction 1 [1.24 g; bp 30–40 °C (0.10 torr)] to be mainly **1d** but to contain small amounts of the second and third components. The second fraction [1.08 g; bp 90–96 °C (0.20 torr)] contained 12% **1d**, 4% of component two, 8% of component three, and 74% **4**.

The component responsible for the fourth peak was shown to be **4**: 0.80 g (4.21 mmol, 3% based on magnesium); IR (CCl_4) 3610 (OH), 1634 (C=C) cm^{-1}; ^{1}H NMR (CCl_4) δ 1.27–1.94 (m, 6, $CHCH_2CH_2CH_2$), 2.31 (s, 1, OH), 2.97–3.28 (m, 1, CHPh), 3.34–3.61 (m, 2, CH_2O), 4.76–5.18 (c, 2, =CH_2), 5.64–6.27 (m, 1, =CH), 7.06–7.33 (m, 5, aryl H's) (this resembled the reported ^{1}H NMR spectrum[6]); low-resolution mass spectrum, m/z (relative intensity) 190 (7), 161 (5), 142 (7), 133 (10), 118 (14), 117 (100), 119 (5), 116 (7), 115 (19), 91 (19); high-resolution mass spectrum, m/z 190.1364 (M$^+$, calcd for $C_{13}H_{18}O$ 190.1357).

The component responsible for the second peak was not identified. The retention time of this component was similar to that of 1-allyl-3-methylcyclopentane. However, the (weak) IR and ^{1}H NMR spectra showed some absorptions characteristic of an aromatic ring.

The third peak seemed to be due to more than one compound. The ^{1}H NMR spectrum showed only weak aryl H absorption. Much of the absorption was consistent with the presence of 6-hepten-1-ol as a major component. This compound has already been noted in reactions of allyl Grignard reagents in THF.[13] The infrared spectrum showed O–H stretching absorption.

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Registry No. 1a, 1745-81-9; **1c**, 3698-28-0; **1d**, 300-57-2; **2a**, 51796-03-3; **2b**, 78167-58-5; **3a**, 78167-59-6; **3c**, 78167-60-9; **3d**, 78167-61-0; **4**, 23431-45-0; allyl chloride, 107-05-1; allyl bromide, 106-95-6; 3-chloro-2-methyl-1-propene, 563-47-3; 1-allyl-3-methylcyclopentene, 78167-62-1.

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