4.75 (1 H, d, J = 2 Hz), 7.0-7.5 (5 H, m).

2-Methylcyclohexanone trimethylsilyl enol ether (9) was prepared as above followed by distillation through a spinning-band column to separate the 79:21 mixture of **9** and **10**: ^{1}H NMR ($CDCl_3$) δ 0.2 (9 H, s), 1.53 (3 H, s, and 4 H br m), 1.9 (4 H, br m).

2-Methylcyclohexanone trimethylsilyl enol ether (10) was prepared by reaction of 2-methylcyclohexanone with lithium diisopropylamide at -78 °C in THF followed by addition of trimethylchlorosilane. Distillation of the product through a spinning-band column gave material of 99% purity by GLC: ^{1}H NMR ($CDCl_3$) δ 0.2 (9 H, s), 1.0 (3 H, d, J = 7 Hz), 1.5 (4 H, m), 1.95 (4 H, m), 4.66 (1 H, t, J = 4 Hz).

Cyclohexanone *tert*-butyldimethylsilyl enol ether (8) was prepared by reaction of cyclohexanone (18.6 g, 200 mmol) with lithium diisopropylamine (200 mmol) at 0 °C in THF (200 mL) followed by addition of *tert*-butyldimethylchlorosilane (32.9 g, 210 mmol). Short-path distillation of the product gave a 75% yield of the enol ether: ^{1}H NMR ($CDCl_3$) δ 0.1 (6 H, s), 0.9 (9 H, s), 1.4-1.7 (4 H, m), 1.8-2.2 (4 H, m), 4.8 (1 H, m).

Preparation of Acetyl Fluoride. Acetyl fluoride was prepared by reaction of acetyl chloride with anhydrous KF in acetic acid solution as previously described.[11] Greater than 98% yields of distilled material [bp 20 °C (745 mm)] were routinely obtained.

Acylation of Ketone Silyl Enol Ethers (Procedure A). Acetyl tetrafluoroborate was prepared by reaction of boron trifluoride with acetyl fluoride at 0 °C in the absence of solvent as previously described.[12] A 50-mL flask with a septum inlet and magnetic stirring bar was flushed with argon and charged with 1.49 g (11.5 mmol) acetyl tetrafluoroborate. The flask was immersed in a nitromethane-dry ice slush bath at -35 °C, and 23 mL nitromethane was injected. The silyl enol ether (11.5 mmol) was added dropwise to the solution, and the mixture was stirred for 1 h at -35 °C and then allowed to reach room temperature. The solution was quenched with 5 mL of saturated aqueous sodium acetate and refluxed for 2 h. The cooled aqueous layer was then extracted twice with ether. The combined organic extract was dried over sodium sulfate and analyzed by GLC for C-acylated ketone. Samples for spectral examination were obtained by preparative GLC.

Acylation of Ketone Silyl Enol Ethers (Procedure B). A 50-mL flask with septum inlet and mercury bubbler was flushed with argon and charged with 23 mL nitromethane and 11.5 mmol (0.714 g) acetyl fluoride. The flask was immersed in a cooling bath maintained at -35 °C. After the mixture was stirred for 10 min, BF_3 gas (1.15 mmol, 27 mL was added by means of a gas-tight syringe. The silyl enol ether (11.5 mmol) was then injected into the reaction solution all at once. The solution was allowed to stir for 1 h and then worked up as described for procedure A above.

2-Acetylcyclohexanone was prepared from cyclohexanone trimethylsilyl enol ether by procedure A: ^{1}H NMR ($CDCl_3$) δ 1.70 (4 H, m), 2.05 (3 H, s), 2.31 (4 H, m), 15.2 (1 H, s); mass spectrum, m/e (relative intensity) 140 (M^+, 30) 125 (49), 97 (26), 69 (29), 55 (31), 43 (100).

3-Methyl-2,4-hexanedione was prepared from 3-pentanone trimethylsilyl enol ether by procedure A: ^{1}H NMR ($CDCl_3$) δ 1.0 (3 H, t, J = 7 Hz), 1.21 (3 H, d, J = 8 Hz), 2.15 (3 H, s), 2.45 (2 H, q, J = 7 Hz), 3.75 (1 H, q, J = 8 Hz), 16.3 (1 H, s).

3,3,5-Trimethyl-2,4-hexanedione was prepared from 2,4 dimethyl-3-pentanone trimethylsilyl enol ether by procedure B: ^{1}H NMR ($CDCl_3$) δ 1.03 (6 H, d, J = 7 Hz), 1.33 (6 H, s), 2.06 (3 H, s), 2.86 (1 H, septet, J = 7 Hz).

2-Acetylcyclopentanone was prepared from cyclopentanone trimethylsilyl enol ether by procedure A: ^{1}H NMR ($CDCl_3$) δ 1.96 (3 H, s), 1.64-2.72 (6 H, m), 2.20 (s), 3.3 (m), 13.8 (br s).

4-Phenyl-2,4-hexanedione was prepared from acetophenone trimethylsilyl enol ether by procedure A: ^{1}H NMR ($CDCl_3$) δ 2.1 (3 H, s), 4.0 (s), 6.07 (s), 7.2-7.9 (5 H, m).

2-Acetyl-6-methylcyclohexanone was prepared by 2-methylcyclohexanone trimethylsilyl enol ether **9** by procedure A: ^{1}H NMR ($CDCl_3$) δ 1.17 (3 H, s), 1.5-1.8 (4 H, m), 2.08 (3 H, s) 2.0-2.5 (3 H, m), 12.5 (1 H, s).

2-Acetyl-2-methylcyclohexanone was prepared from 2-methylcyclohexanone trimethylsilyl enol ether **10** by procedure B: ^{1}H NMR ($CDCl_3$) δ 1.23 (3 H, s), 1.45-1.9 (6 H, m), 2.08 (3 H, s), 2.2-2.6 (2 H, m).

Acknowledgement is made to the National Science Foundation for partial support of this work.

Registry No. **4**, 6651-36-1; **5**, 874-23-7; **6**, 1424-22-2; **8**, 62791-22-4; **9**, 19980-35-9; **10**, 19980-33-7; **11**, 17510-47-3; **12**, 55339-64-5; **13**, 19980-43-9; **14**, 13735-81-4; trimethylchlorosilane, 75-77-4; cyclohexanone, 108-94-1; 3-pentanone, 96-22-0; 2,4-dimethyl-3-pentanone, 565-80-0; cyclopentanone, 120-92-3; acetophenone, 98-86-2; 2-methylcyclohexanone, 583-60-8; *tert*-butyldimethylchlorosilane, 18162-48-6; acetyl fluoride, 557-99-3; acetyl chloride, 75-36-5; acetyl tetrafluoroborate, 2261-02-1; 3-methyl-2,4-hexanedione, 4220-52-4; 3,3,5-trimethyl-2,4-hexanedione, 42412-60-2; 2-acetylcyclopentanone, 1670-46-8; 1-phenyl-1,3-butanedione, 93-91-4; 2-acetyl-6-methylcyclohexanone, 78456-49-2; 2-acetyl-2-methylcyclohexanone, 1195-75-1; 3-acetoxy-2,4-dimethyl-2-pentene, 4007-46-9.

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Reactions of Allylic Grignard Reagents and Unsaturated Amines[1]

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Reactions were studied of allylic Grignard reagents with allylic and propargylic amines. Additions were observed to *N*-allylaniline (**1**), cinnamylamine (**6**), *N,N*-dimethylcinnamylamine (**10**), and 3-(dimethylamino)-1-phenyl-1-propyne (**12**) but not to allylamine, diallylamine, *N*-allyl-*N*-methylaniline, *N,N*-dimethylallylamine, or *N,N*-diethylallylamine. Reactions of 3-amino-1-phenyl-1-propyne (**8**) furnished phenylacetylene rather than an addition product. By comparing reactivities of the amines and comparable hydrocarbons, it is concluded that tertiary amino functions and metalated primary and secondary amino functions can assist Grignard reagent additions to alkene and alkyne functions. Comparisons of reactivities of the unsaturated amines and comparable alcohols suggest that assistance by a metalated amino function is less effective than by a metalated hydroxyl function but more effective than by a tertiary amino function. Another comparison suggests that a metalated phenylamino group is more effective than a metalated primary amino group.

Eisch[5] and Felkin[6] observed that allylic organomagnesium compounds (in excess) add to alkenols. For example, allylmagnesium bromide and allyl alcohol form a good yield of an addition product[6] (eq 1). The hydroxyl

0022-3263/81/1946-3773$01.25/0

$$CH_2{=}CHCH_2OH \xrightarrow[2.\ H_2O]{1.\ CH_2{=}CHCH_2MgBr} CH_3CH(CH_2CH{=}CH_2)CH_2OH \quad (1)$$

groups of alkenols certainly are metalated instantaneously by reaction with 1 equiv of an organomagnesium compound. The metalated hydroxyl groups must facilitate additions to the alkene functions since, under comparable conditions, organomagnesium compounds do not add to unstrained, nonconjugated alkenes. A variety of additions of organomagnesium compounds to allylic and homoallylic alkenols[7-12] have since been reported, as have additions to propargylic and homopropargylic alkynols[10,13-15] and allenols.[16]

We decided to investigate whether amino groups could also assist additions to multiple bonds. Assistance by primary or secondary amino groups seemed a likely possibility. Such functions would be rapidly metalated by an organomagnesium compound to form species such as RNHMgX or RNHMgR', isoelectronic with the ROMgX or ROMgR' that must be responsible for the effect of a hydroxyl group. Besides unsaturated primary and secondary amines, we included unsaturated tertiary amines to determine if tertiary amino groups might also facilitate additions. At the time this work was initiated, no additions to unsaturated amines had been reported. We did note, however, that addition products had not been observed in several reactions of Grignard reagents and unsaturated tertiary amines.[17-19]

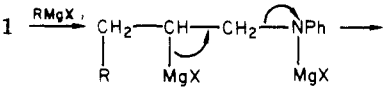
Results

Reactions with Primary and Secondary Amines. Addition compound **2** and aniline (**3**) were products of the reaction of *N*-allylaniline (**1**) and an excess of allylmagnesium chloride in refluxing diethyl ether (eq 2). GC

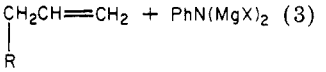
$$\underset{\mathbf{1}}{CH_2{=}CHCH_2NHPh} \xrightarrow[2.\ H_2O]{1.\ CH_2{=}CHCH_2MgCl} \underset{\mathbf{2}}{CH_3CH(CH_2CH{=}CH_2)CH_2NHPh} + \underset{\mathbf{3}}{PhNH_2} \quad (2)$$

analysis showed that their yields increased with time.[20] After 22 h, 25% of **1**, 32% of **2**, and 29% of **3** were present, but following that time, the composition did not change significantly. GC analysis showed that a similar reaction in refluxing tetrahydrofuran (THF) also was relatively slow. After 66 h, 25% of **1**, 44% of **2**, and 16% of **3** were present. In THF at 100 °C, the half-time of the reaction was about 2 h, and after much longer times the composition was 0% **1**, 37% **2**, and 48% **3**.

Aniline probably resulted from addition having the orientation shown in **4**, followed by elimination[21] (see eq 3). This process should also produce 1,5-hexadiene (**5a**).



4



(3)

5a, R = $CH_2{=}CHCH_2$
b, R = $CH_2{=}C(CH_3)CH_2$

We did not search for **5a**, since it is also present as a byproduct of formation of the Grignard reagent from allyl chloride and magnesium. However, the reaction of (2-methyl-2-propenyl)magnesium chloride with **1** should produce **5b**. From such a reaction that was heated at reflux temperature in diethyl ether for 33 h, we detected 7% of **5b**, as well as some of the symmetrical diene 2,5-dimethyl-1,5-hexadiene (a byproduct of Grignard reagent formation) and 72% of aniline. An addition product similar to **2** could have been present only in a relatively small amount.

A reaction of allyl phenyl ether, the oxygen analogue of **1**, with allylmagnesium chloride in refluxing THF furnished a 75% yield of phenol. No addition product was detected. Similar reactions of allylic ethers and Grignard reagents have been observed before.[22]

No addition products were detected after allylamine and an excess of allylmagnesium chloride were heated in diethyl ether at reflux temperature for 2 h, although some 1,5-hexadiene was observed. Similarly, no addition products were detected after the same components were heated in tetrahydrofuran (THF) at reflux temperature for 23 h.

The 1,5-hexadiene is a byproduct of the formation of allylmagnesium chloride from allyl chloride and magnesium. However, some portion of it also could have arisen from an addition followed by an elimination (as shown in **4**). To determine if such an addition–elimination might be significant, we investigated a reaction of allylamine and (2-methyl-2-propenyl)magnesium chloride. No addition product was detected after the reactants were heated in diethyl ether at reflux temperature for 24 h, and the only diene obtained was 2,5-dimethyl-1,5-hexadiene, a bypro-

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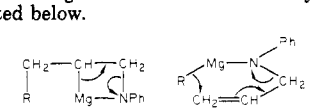
(18) Mauzé, B.; Courtois, G.; Miginiac, L. *C. R. Hebd. Seances Acad. Sci., Ser. C* **1969**, *269*, 1225.

(19) A reaction of 4-(phenylamino)-4,4-diphenyl-1-butene and allylmagnesium bromide furnished products of cleavage of the amine rather than of addition to the double bond: Eisch, J. J.; Harrell, R. L., Jr. *J. Organomet. Chem.* **1970**, *21*, 21.

(20) See the Experimental Section for a description of the procedure and the assumptions used in determining yields by GC analysis.

(21) This product might also have arisen from cyclic processes, such as those illustrated below.



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duct of formation of the Grignard reagent. An addition–elimination sequence would have produced 2-methyl-1,5-hexadiene (**5b**).

Allylamine was not recovered in significant amounts from these reactions, presumably because it remained in the aqueous layers resulting from hydrolysis. However, nearly as much allylamine was recovered in the form of its *p*-toluenesulfonyl derivative from reactions in refluxing ether (62% and 81%) as from a control experiment (86%) in which no Grignard reagent was used.

After diallylamine and (2-methyl-2-propenyl)magnesium chloride were heated in THF at reflux temperature for 24 h, some of the amine remained, but a considerable portion had reacted in some fashion.[23] However, the components detected by GC analysis were present in only small amounts. Even smaller amounts of the amine and of other volatile components were detected in the materials obtained from reactions at 100 °C.

Compound **7** was isolated in 23% yield from a reaction of cinnamylamine (**6**) and allylmagnesium chloride in refluxing THF for 17 h (eq 4). A similar reaction of allyl-

$$\underset{\mathbf{6}}{\mathrm{PhCH{=}CHCH_2NH_2}} \xrightarrow[2.\ H_2O]{1.\ CH_2{=}CHCH_2MgCl} \underset{\mathbf{7}}{\mathrm{PhCH_2CH(CH_2CH{=}CH_2)CH_2NH_2}} \quad (4)$$

magnesium chloride with an equimolar mixture of **6** and 1-phenyl-1-propene gave a considerable amount of **7**. However, no product of addition to 1-phenyl-1-propene was detected, suggesting that addition to **6** is at least 10 times faster than to the hydrocarbon.

The amine was reisolated in 40% yield,[20] and no new products were detected after 3-amino-1-phenyl-1-propyne (**8**) and allylmagnesium chloride were left in THF at ambient temperature for 21 h. However, after a similar reaction mixture was refluxed for 21 h, 44%[20] of phenylacetylene (**9**) was found (see eq 5), and **8** was not detected.

$$\underset{\mathbf{8}}{\mathrm{PhC{\equiv}CCH_2NH_2}} \xrightarrow[2.\ H_2O]{1.\ RMgX} \underset{\mathbf{9}}{\mathrm{PhC{\equiv}CH}} \quad (5)$$

Similarly, **8** was not detected and **9** was the only significant new product after **8** and butylmagnesium bromide were heated in refluxing THF.

Reactions with Tertiary Amines. No addition products were observed after allylmagnesium chloride was heated with *N*-allyl-*N*-methylaniline in refluxing diethyl ether for 48 h or with *N*,*N*-dimethylallylamine or *N*,*N*-diethylallylamine in refluxing THF for 8 h. Allylmagnesium chloride was prepared directly in toluene containing 1 equiv of *N*,*N*-diethylallylamine. After this solution had been refluxed for 18 h, the amine was reisolated in 62% yield. A small amount of other basic material was present, but it did not exhibit the ^{1}H NMR absorptions expected for an addition product.

Compound **11** was isolated in 44% yield from a reaction of *N*,*N*-dimethylcinnamylamine (**10**) and allylmagnesium chloride in refluxing toluene–THF for 40 h (eq 6). Small

$$\underset{\mathbf{10}}{\mathrm{PhCH{=}CHCH_2NMe_2}} \xrightarrow[2.\ H_2O]{1.\ CH_2{=}CHCH_2MgCl} \underset{\mathbf{11}}{\mathrm{PhCH_2CH(CH_2CH{=}CH_2)CH_2NMe_2}} \quad (6)$$

amounts of products resulting from further addition to **11** may also have been present. A considerable amount of **11** was obtained, and no product of addition to 1-phenyl-1-propene were detected in a similar reaction of allylmagnesium chloride with an equimolar mixture of **10** and the hydrocarbon. The results suggest that addition to **10** is at least 10 times faster than to 1-phenyl-1-propene. Only small amounts of **11** were obtained from a reaction of **10** and allylmagnesium chloride in refluxing THF (without the toluene). The reactant was reisolated in good yield, and no addition products were detected in a reaction of **10** and butylmagnesium chloride in refluxing methylcyclohexane for 8 h.

Compound **13** was isolated in 49% yield from a reaction of 3-(dimethylamino)-1-phenyl-1-propyne (**12**) and allylmagnesium chloride in refluxing THF for 20 h (eq 7). The

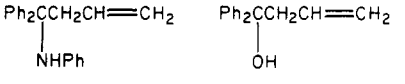
$$\underset{\mathbf{12}}{\mathrm{PhC{\equiv}CCH_2NMe_2}} \xrightarrow[2.\ H_2O]{1.\ CH_2{=}CHCH_2MgCl} \underset{\mathbf{13}}{\mathrm{PhCH{=}C(CH_2CH{=}CH_2)CH_2NMe_2}} \quad (7)$$

configuration of **13** was not determined. Some **13** was formed, but no products of addition to 1-phenyl-1-butyne were detected in a similar reaction of allylmagnesium chloride with an equimolar mixture of **12** and the hydrocarbon. The result is consistent with addition to **12** being at least 5 times faster than to 1-phenyl-1-butyne.

Discussion

The results demonstrate that tertiary amino groups and metalated primary and secondary amino groups can assist addition of organomagnesium compounds to alkene and alkyne functions. Addition to primary amine **6** and to tertiary amines **10** and **12** was in each instance faster than to a comparable unsaturated compound that lacked the amino group. Similarly, addition to secondary amine **1** was faster than previously reported additions to unbranched 1-alkenes.[24] In studies with unsaturated alcohols, we found that a metalated hydroxyl group constrained to a position that prevents it from approaching the double bond actually slows additions of an allylmagnesium compound.[11] Therefore, it is likely that the accelerating effect of the amino groups is due to their direct involvement in the addition process rather than to some property such as an inductive effect.

Several comparisons with additions to alcohols indicate that assistance by a metalated amino group is less effective than that offered by a metalated hydroxyl group. Eisch and Merkley have already reported that allylmagnesium bromide does not add to secondary amine **14** when con-



14 **15**

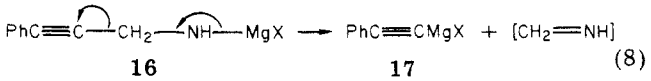
ditions are used which cause addition to take place to **15**.[9] In the work reported in this paper, addition of allylmagnesium chloride or (2-methyl-2-propenyl)magnesium chloride to allylamine was not observed, and that to *N*-allylaniline was slow when conditions were used that lead to a ready addition of allylmagnesium bromide to allyl alcohol.[6,25] Similarly, a significant amount of **8** was recovered from a reaction with allylmagnesium chloride under conditions which lead to significant additions to $CH_3C{\equiv}CCH_2OH$.[26] Phenylacetylene (**9**), the only product

(23) Perhaps this was by cleavage, as observed[19] with another compound, followed by other reactions.

(24) Lehmkuhl, H.; Reinehr, D.; Schomburg, G.; Henneberg, D.; Damen, H.; Schroth, G. *Justus Liebigs Ann. Chem.* **1975**, 103. Lehmkuhl, H.; Janssen, E. *Ibid.* **1978**, 1854.

(25) The difference between allylmagnesium bromide and allylmagnesium chloride is not expected to be significant. In reactions with 4-hexyn-2-ol, the chloride actually adds somewhat faster than the bromide.[26]

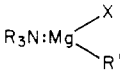
noted from reactions of 8 and Grignard reagents, presumably formed by a cleavage such as 16 → 17[27] (eq 8). The



16 17 (8)

readier addition to cinnamylamine (6) than to allylamine must result from the same effect of phenyl that makes addition to cinnamyl alcohol faster than to allyl alcohol.

The observation that addition to tertiary amine 10 was much slower than to the corresponding primary amine (6) suggests that a tertiary amino group assists additions less effectively than does a metalated amino group. The rate of addition to tertiary amine 12 cannot similarly be compared to that of the corresponding primary amine (8) since 8 underwent fragmentation rather than addition. Mornet and Gouin have recently reported additions of alkylmagnesium halides to propargylic amines, $RC{\equiv}CCH_2NR'_2$ (R and R′ are alkyl), at 100–110 °C in toluene.[15,28] The assistance by tertiary amino groups must be ascribed to complexes such as 18 with organomagnesium compounds.



18

In such complexes, MgX or MgR′ could have relationships to the multiple bonds similar to those in metalated alcohols (ROMgX and ROMgR′) or amines.

The observations that allylmagnesium chloride in either refluxing diethyl ether or THF solutions adds to 1 but not to allylamine suggest that the allylic metalated NHPH group is more effective than an allylic metalated NH_2 group in assisting addition. This conclusion and the greater effectiveness of metalated hydroxyl groups than of metalated amino groups are both consistent with the idea that effectiveness in assisting additions increases with decreasing basicity of the metalated assisting atom. Another observation consistent with this conjecture is reported in an accompanying paper.[29]

We conclude that amino functions can assist additions of organomagnesium compounds to alkene and alkyne functions. From those comparisons that can be made, a metalated amino function is less effective than a metalated hydroxyl function but more effective than a tertiary amino function. We must note that the comparisons have involved only allylic organomagnesium compounds, and the conclusions may not extend to other organomagnesium compounds. For a number of reasons, allylic organomagnesium compounds may be atypical. For example, reactions of the allylic group can take place at the γ-carbon, a possibility that does not exist for most other groups. Moreover, with the exception of the comparison of 14 with 15, all comparisons have involved allylic or propargylic amines and therefore may not be general for unsaturated amines having greater separation between the amino and unsaturated functions. There are indications that additions of allylic organomagnesium compounds to homoallylic alcohols proceed differently than to allylic alcohols.[11]

Experimental Section

^1H NMR spectra were taken at 60 MHz. Sodium 2,2-dimethyl-2-silapentane-5-sulfonate was used as an internal standard in the trifluoroacetic acid solutions and Me_4Si in all others. Absorptions are reported with the following notations: s, singlet; d, doublet; t, triplet; q, quartet; m, a more complex multiplet; c, complex overlapping absorptions. IR spectra (calibrated with a polystyrene film) and low-resolution mass spectra, though not generally reported in this paper, were taken of many compounds; some data are given in ref 3. High- and low-resolution mass spectra were obtained by using an AEI Model MS 902 spectrometer and an ionization potential of 70 eV. Melting points were taken in capillary tubes and are uncorrected. Microanalyses were performed by Midwest Microlab, Ltd.

Analytical and preparative GC separations were performed with thermal conductivity instruments using helium as the carrier gas and the following columns: A, 20% SF-96 on gas Chrom Z (60–80 mesh), 0.25 in. × 5 ft (aluminum tubing); B, 20% SE-30 on Chromosorb W (60–80 mesh), 0.25 in. × 5 ft (copper tubing); C, 20% Versamid 900 on Gas Chrom P (60–80 mesh), 0.25 in. × 10 ft (aluminum tubing); D, 15% XE-60 on Gas Chrom Q (80–100 mesh), 0.25 in. × 6 ft (aluminum tubing); E, 20% SE-30 on Gas Chrom Q (80–100 mesh), 0.25 in. × 10 ft (aluminum tubing); F, 5% SE-30 on Gas Chrom P (80–100 mesh), 0.25 in. × 5 ft (aluminum tubing). Peak areas were ordinarily determined by using a planimeter. When amounts of components of a crude (undistilled) reaction mixture were determined by GC analysis, a weighed amount of a normal alkane was added as a standard. An alkane was chosen whose GC peak was known from preliminary work not to overlap with those of components of the reaction mixture. The amount of a component was determined from the area of its GC peak relative to the peak due to the standard by assuming that the response of the detector to different compounds was proportional to their molecular weights. In the GC analysis of a distillation fraction, it was sometimes assumed that all of the material appeared in one of the observed peaks (a reasonable assumption since materials having little volatility had already been removed).

Materials. (a) Substrates for Reactions with Organomagnesium Compounds. *N*-Allylaniline (1), allyl phenyl ether, allylamine, diallylamine, *N*-allyl-*N*-methylaniline, *N*,*N*-dimethylallylamine, and *N*,*N*-diethylallylamine were commercial samples and were distilled before use. The hydrochloride of cinnamylamine was prepared as already described[30] and then converted to the free amine 6, bp 66–73 °C (0.15 torr) [lit.[31] bp 235–237 °C (775 torr)]. A sample of 3-chloro-1-phenyl-1-propyne was prepared as already described;[32] bp 87–95 °C (4 torr) [lit.[32] bp 99 °C (7 torr)]. This chloride was converted to the hydrochloride of 3-amino-1-phenyl-1-propyne by using a procedure described for the preparation of cinnamylamine hydrochloride.[30] The hydrochloride was then converted to the free amine 8: bp 65–66 °C (0.35 torr); (only the hydrochloride of 8 has been previously reported[33]); IR (CCl_4) 3390, 3330 (NH_2) cm^{-1}; ^1H NMR (CCl_4) δ 1.32 (s, 2, disappears on shaking with D_2O, NH_2), 3.52 (s, 2, CH_2), 7.24 (m, 5, Ph). *N*,*N*-Dimethylcinnamylamine (10) was prepared by using a procedure[34] used to prepare the corresponding hydrochloride. After filtration of the precipitated dimethylamine hydrobromide, the diethyl ether solution was washed three times with a saturated sodium bicarbonate solution and dried ($MgSO_4$). Distillation gave 10, bp 55–60 °C (0.3 torr) [lit.[35] bp 100–101 °C (7 torr)]. A sample of 3-(dimethylamino)-1-phenyl-1-propyne (12) was prepared as already described;[17] bp 95–97 °C (5 torr) [lit.[17] bp 105–106 °C (0.8 torr)].

(b) Organomagnesium Compounds. Solutions of allylic Grignard reagents were prepared in a manner similar to that described for the preparation of allylmagnesium chloride in diethyl

(26) Von Rein, F. W. Ph.D. Dissertation, The Pennsylvania State University, University Park, PA, 1972.

(27) Conceivably, a dimetalated species such as $PhC{\equiv}CCH_2N(MgX)_2$ is involved. Compare this to the reactions of organolithium compounds with primary amines: Richey, H. G., Jr.; Erickson, W. F.; Heyn, A. S. *Tetrahedron Lett.* **1971**, 2187. Erickson, W. F.; Richey, H. G., Jr. *Ibid.* **1972**, 2811.

(28) Additions have also been observed to compounds of structure $R_2NCH_2C{\equiv}CCH_2X$ where X is OH, OR′, SR′, or NR'_2:[15] Mornet, R.; Gouin, L. *J. Organomet. Chem.* **1975**, *86*, 57, 297. Mornet, R.; Gouin, L. *Ibid.* **1977**, *135*, 151.

(29) Richey, H. G., Jr.; Domalski, M. S. *J. Org. Chem.*, following paper in this issue.

(30) Gensler, W. J.; Rockett, J. C. *J. Am. Chem. Soc.* **1955**, *77*, 3262.

(31) Posner, T. *Chem. Ber.* **1893**, *26*, 1856.

(32) Murray, M. J. *J. Am. Chem. Soc.* **1938**, *60*, 2662.

(33) Simon, D. Z.; Salvador, R. L.; Champagne, G. *J. Med. Chem.* **1970**, *13*, 1249.

(34) Mitsch, R. A.; Crowmwell, N. H. *J. Org. Chem.* **1960**, *25*, 1719.

(35) Braun, J. v.; Köhler, Z. *Chem. Ber.* **1918**, *51*, 79.

ether.[36] The yields, often determined by a double titration procedure,[37] were generally in the range 55–65%. Commercial (Ventron Corp.) solutions of allylmagnesium chloride in THF were used where noted. A commercial solution (Ventron Corp.) of butylmagnesium chloride in diethyl ether was used.

(c) Other Compounds. Allyl chloride and 3-chloro-2-methyl-1-propene were distilled and then stored over molecular sieves (4A or 5A). The magnesium was Fisher Scientific turnings or J. T. Baker analyzed reagent. THF was distilled from $LiAlH_4$ under a nitrogen atmosphere. Diethyl ether and toluene were stored over sodium and alkanes over molecular sieves (4A or 5A).

Procedure for Reactions with Grignard Reagents. Except where otherwise noted, the following procedure was used. Reactions were carried out in standard-taper, three-necked, round-bottomed flasks containing a magnetic stirring bar and fitted with a condenser having a gas inlet tube at the top, a pressure-equalizing addition funnel, and, if a commercial solution of Grignard reagent was to be used, a rubber septum. Glassware was stored at 120 °C prior to assembly; after assembly (and addition of magnesium if the Grignard reagent was to be prepared), the apparatus was heated gently with a Bunsen burner while nitrogen was flowing rapidly through it. During the course of a reaction, a positive pressure of nitrogen was maintained in the closed reaction system.

Either the Grignard reagent was prepared in this assembly or a solution of commercial Grignard reagent was added through the serum stopper. Gas-tight syringes were used for all transfers of Grignard reagent solutions and anhydrous solvents. A solution of the unsaturated substrate was added slowly (15–30 min) to the stirred solution of Grignard reagent which was cooled in an ice bath.

Some reaction mixtures were left in this assembly and heated as specified. Others were heated at 100 °C in ampules. Several glass ampules, stored at 110 °C prior to use, were attached with Tygon tubing to a manifold which then was evacuated and filled with nitrogen several times. The manifold had an opening covered with a rubber septum above the open end of each ampule. A gas-tight syringe with a long needle was used to fill each ampule through the septum. The ampules were partially evacuated and then cooled in liquid nitrogen prior to being sealed. The ampules were allowed to thaw and placed in a constant-temperature bath maintained at 100.0 °C.

After the desired reaction time, the flask or the contents of several ampules were cooled in an ice bath. Hydrolysis was ordinarily done by using one of the following procedures. (A) Water was added slowly, followed by a saturated ammonium chloride solution to dissolve the precipitate. The layers were separated, and the aqueous layer was extracted twice with diethyl ether. The combined organic layers were washed with a saturated sodium bicarbonate solution and then dried ($MgSO_4$). (B) Water was added slowly and then the mixture was filtered. The filtrate was washed three times with a saturated sodium bicarbonate solution and dried ($MgSO_4$).

After removal of most of the solvent, the residue was either distilled at reduced pressure or subjected to GC analysis. A component that constituted more than 2% of a reaction mixture or distillation fraction would generally have been detected by the GC analysis. Small samples of each significant component were collected for spectral analysis by using glass U-shaped tubes inserted into the exit port of the gas chromatograph and cooled in liquid nitrogen.

The progress with time of some reactions was followed. An ampule was removed from the constant-temperature bath, cooled, opened, and fitted with a rubber septum. A saturated ammonium chloride solution was added by using a syringe, and the organic layer was subjected to GC analysis. Alternatively, an aliquot was removed from the reaction flask and treated in a similar fashion.

Reaction of *N*-Allylaniline (1). (a) With Allylmagnesium Chloride in Diethyl Ether. A solution of 1 (2.46 g, 18 mmol) in diethyl ether (25 mL) was added to a Grignard reagent solution prepared from allyl chloride (6.18 g, 81 mmol) and magnesium (2.13 g, 88 mmol) in diethyl ether (70 mL). The resulting solution was refluxed. GC analysis (column E, 202 °C) of aliquots showed the presence of three major components that, as described below, were shown to be **3**, **1**, and **2** (retention times relative to tridecane of 0.34 for **3**, 0.76 for **1**, and 1.92 for **2**). The amounts of **2** and **3** increased with time. After 3 h, the composition was 76% **1**, 10% **2**, and 6% **3** and after 22 h, 25%, 32%, and 29%, respectively. The composition did not change significantly after 22 h. After a total of 48 h, the remainder of the solution was worked up by using procedure A and the resulting diethyl ether solution combined with the diethyl ether layers from the aliquots. Distillation gave a fraction [0.37 g; bp 26–30 °C (0.10 torr)] shown by GC analysis to be 65% **3** (0.24 g, 2.58 mmol, 14% yield) and 35% **1** (0.13 g). The ^1H NMR spectra of the materials responsible for the two GC peaks were identical with those of authentic **3** and **1**. Further distillation gave a fraction [1.36 g; bp 68–71 °C (0.17 torr)] which was shown by GC analysis to be 20% **1** (0.27 g, total of 3.0 mmol from both fractions, 16% yield) and 80% **2** (1.09 g, 6.23 mmol, 34%): IR (CCl_4) 3405 (NH), 1640 (C=C) cm^{-1}; ^1H NMR (CCl_4) δ 0.93 (d, 2, J = 5 Hz, CH_3), 1.43–2.33 (c, 3, $CHCH_2CH$=), 2.73–3.00 (m, 2, CH_2N), 3.44 (br s, 1, NH), 4.88–5.22 (c, 2, =CH_2), 5.30–5.97 (m, 1, =CH), 6.23–6.65 (c, 3, ortho and para aromatic H's), 6.74–7.18 (m, 2, meta aromatic 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 (6), 106 (100), 105 (11), 104 (14), 93 (23), 77 (71); high-resolution mass spectrum, m/z 175.1400 (M^+, calcd for $C_{12}H_{17}N$ 175.1360).

(b) With Allylmagnesium Chloride in THF. A solution of 1 (0.638 g, 4.8 mmol) in THF (25 mL) was added to a Grignard reagent solution prepared from allyl chloride (3.11 g, 41 mmol) and magnesium (1.02 g, 42 mmol) in THF (45 mL). The resulting solution was refluxed. GC analysis as above of aliquots showed the presence of **1**–**3**. The identities of the compounds were established by their retention times and, for **2** and **3**, by their IR and ^1H NMR spectra. The following compositions (for **1**–**3**, respectively) were observed: 1 h, 98%, 0%, and 0%; 20 h, 70%, 11%, and 6%; 41 h, 46%, 29%, and 10%; 66 h, 25%, 44%, and 16%.

Aliquots of a similar solution prepared from addition of 1 to an allylmagnesium chloride solution were sealed in glass ampules which were then heated at 100 °C. GC analysis showed the following compositions (for **1**–**3**, respectively): 1 h, 60%, 12%, and 12%; 2 h, 35%, 20%, and 27%; 4.5 h, 10%, 32%, and 38%; 17 h, 0%, 37%, and 47%; 72 h, 0%, 37%, and 48%.

(c) With (2-Methyl-2-propenyl)magnesium Chloride in Diethyl Ether. A solution of 1 (0.920 g, 6.9 mmol) in diethyl ether (10 mL) was added to a Grignard reagent solution prepared from 3-chloro-2-methyl-1-propene (5.74 g, 63 mmol) and magnesium (1.55 g, 6.4 mmol) in diethyl ether (50 mL). The resulting solution was refluxed for 33 h. GC analysis (column E, 220 °C) of an aliquot showed three major peaks. The first two (retention times relative to tridecane of 0.32 and 0.68) were shown to be due, respectively, to **3** (72% yield) and **1** (4%). The third component (retention time relative to tridecane of 2.03) may have been due to an addition product (7% yield if its molecular formula was $C_{13}H_{19}N$), but it was not investigated. After workup of the entire reaction mixture by use of procedure A, the resulting diethyl ether solution was concentrated by distilling away much of the solvent with a Vigreux column. GC analysis (column E, 80 °C) of the remaining solution showed four peaks past that due to diethyl ether. The first two peaks (retention times relative to heptane of 0.41 and 0.56) were small, and the compounds responsible for them were not investigated. The compounds responsible for the third and fourth peaks (retention times relative to heptane of 0.83 and 1.68) were shown by comparison of their IR and ^1H NMR spectra with those of authentic samples to be **5b** (7% yield) and 2,5-dimethyl-1,5-hexadiene.

Reaction of Allyl Phenyl Ether with Allylmagnesium Chloride in THF. A solution of the ether (2.54 g, 19 mmol) in THF (20 mL) was added to a Grignard reagent solution prepared from allyl chloride (9.68 g, 126 mmol) and magnesium (3.03 g, 125 mmol) in THF (55 mL). The mixture was refluxed for 24 h. After workup by use of procedure A, distillation gave a fraction [1.89 g; bp 43–49 °C (1.5 torr)] shown by GC analysis (column E, 183 °C) to have two components (retention times relative to tridecane of 0.098 and 0.28). The component responsible for the first peak (10% of the total peak area) was not identified. The component responsible for the second peak (90% of peak area)

(36) Kharasch, M. S.; Fuchs, C. F. *J. Org. Chem.* **1944**, *9*, 359.
(37) Vlismas, T.; Parker, R. D. *J. Organomet. Chem.* **1967**, *10*, 193.

was shown by its IR and ^1H NMR spectra to be phenol (75% yield). No allyl phenyl ether (relative retention time about 3.7) was detected.

Reactions of Allylamine. (a) With Allylmagnesium Chloride; Isolation of the *p*-Toluenesulfonyl Derivative of Allylamine. The Grignard reagent solution (47 mmol) was prepared from allyl chloride (7.65 g, 100 mmol) and magnesium (2.70 g, 111 mmol) in diethyl ether (107 mL), and its concentration was determined by hydrolysis and titration for base. A solution of the amine (0.685 g, 12.0 mmol) in diethyl ether (20 mL) was added, and the reaction mixture was refluxed for 2 h and then hydrolyzed by addition of water (230 mL). The contents of the flask were heated and distilled into another flask until all of the ether and about 50 mL of water had distilled. The distillate was acidified with sulfuric acid, and the diethyl ether was removed at reduced pressure. The solution was made slightly basic by addition of a sodium hydroxide solution. Then *p*-toluenesulfonyl chloride (2.44 g, 13 mmol) and sodium hydroxide (0.96 g, 24 mmol) were added, and the suspension was stirred for 1 h. The same amounts of the sulfonyl chloride and sodium hydroxide were added again, and stirring was continued for 1.5 h more. Half of the previous amounts were then added, followed by stirring for 0.5 h more, and then half portions were added again and stirring continued for another 1.5 h. The suspension was heated to 55 °C, and more sodium hydroxide (4.0 g) was added. The suspension was stirred at this temperature for 0.5 h, eventually forming a clear solution. The solution was cooled to ambient temperature, acidified to pH 2–3 with hydrochloric acid, and extracted with three 100-mL portions of diethyl ether. The organic extracts were washed with water and dried ($MgSO_4$). The solvent was removed at reduced pressure, and the oily residue was left in a desiccator over phosphorus pentoxide. The crude solid that resulted (1.57 g, 7.4 mmol, 62%) was essentially pure *N*-allyl-*p*-toluenesulfonamide. In a similar reaction in which only half as much Grignard reagent was used, the amide was isolated in 81% yield.

In a typical control reaction, *p*-toluenesulfonyl chloride (6.1 g, 32 mmol) and sodium hydroxide (2.4 g, 60 mmol) were added to a solution of the amine (1.71 g, 30 mmol) in water (150 mL), and the suspension was stirred for 1 h. The same amounts of the sulfonyl chloride and sodium hydroxide were added again, and stirring was continued for 0.5 h more. Then half portions were added, followed by stirring for 1 h, and half portions were again added and stirring continued for 0.5 h. The suspension was heated to 55 °C, and more sodium hydroxide (10 g) was added. The suspension was stirred at this temperature for 0.5 h, forming a clear solution. The remainder of the procedure was exactly as described above. The crude solid (5.48 g, 26 mmol, 86%) had a ^1H NMR spectrum essentially identical with that of an authentic sample of *N*-allyl-*p*-toluenesulfonamide (prepared from allylamine by using a standard procedure)[38] and a melting point of 55–61 °C (lit.[39] mp 64–65 °C). This procedure for derivatizing allylamine from a dilute aqueous solution was adapted from one used with 1-amino-3-butene.[40] The procedure gave low yields with allylamine until modified to that above, principally by eliminating a wash of the diethyl ether extracts with a 50% potassium hydroxide solution and using magnesium sulfate in place of potassium carbonate as the drying agent.

Another reaction of allylmagnesium chloride and allylamine (ca. 2:1) for 2 h at reflux temperature was worked up by using procedure A. GC analysis (column B) of the residue remaining after removal of most of the solvent at reduced pressure showed the presence of only a small amount of allylamine and the presence of one new peak shown by a ^1H NMR spectrum to be due to 1,5-hexadiene.

A reaction of allylamine and a commercial solution of allylmagnesium chloride in THF for 23 h at reflux temperature was worked up by using procedure A. The oil remaining after removal of the solvent was shown by GC analysis (column D, 130 °C) to contain only two volatile components (relative retention times 1.0 and 1.9). These were shown by their retention times and IR and ^1H NMR spectra to be 2-methyl-4-penten-1-ol and 6-hepten-1-ol. These compounds were present in the same ratio in a control reaction in which the amine was omitted. The 2-methyl-4-penten-1-ol must result from exposure of the commercial Grignard reagent solution to oxygen, resulting in formation of metalated allyl alcohol to which the Grignard reagent then adds.[6] The 6-hepten-1-ol must result from attack on THF.[41]

(b) With (2-Methyl-2-propenyl)magnesium Chloride. A solution of allylamine (0.98 g, 17 mmol) in diethyl ether (15 mL) was added to a Grignard reagent solution prepared from 3-chloro-2-methyl-1-propene (5.77 g, 64 mmol) and magnesium (1.52 g, 63 mmol) in diethyl ether (55 mL). The reaction mixture was refluxed for 24 h and then hydrolyzed by addition of water (6 mL). The organic phase was poured from the flask, the remaining solid was washed several times with diethyl ether, and the combined organic layers were dried ($MgSO_4$). This solution was concentrated by distilling away much of the solvent through a Vigreux column. GC analysis (column E, 100 °C) showed only peaks due to diethyl ether and to one new component (retention times 0.30 and 1.60 relative to heptane). The new component was shown by its IR, ^1H NMR, and mass spectra to be 2,5-dimethyl-1,5-hexadiene. Allylamine (retention time 0.43 relative to heptane) was not detected.

Reactions of Diallylamine with (2-Methyl-2-propenyl)-magnesium Chloride. A solution of the amine (1.49 g, 15 mmol) in THF (20 mL) was added to a Grignard reagent solution prepared from 3-chloro-2-methyl-1-propene (7.34 g, 81 mmol) and magnesium (1.99 g, 82 mmol) in THF (45 mL). The resulting mixture was refluxed for 24 h and worked up by using procedure A. The solvent was removed by distillation through a Vigreux column, leaving an oil (1.15 g). GC analysis (column E, 200 °C) of the residue showed a major peak (~70% of the total peak area), due to diallylamine, and several peaks having longer retention times, the largest of which was only 8% of the total peak area. The ^1H NMR spectrum (CCl_4) showed the residue to contain no more than 30–35% of diallylamine. Presumably the residue contained relatively nonvolatile components that were not eluted from the GC column.

Similar reactions were run by sealing the reaction mixtures in ampules which were then heated at 100 °C. GC analysis of the residues remaining after removal of the solvent from the dark red solutions that resulted showed the presence only of small amounts of diallylamine or of other volatile components. Nothing could be distilled at reduced pressure from these materials, which were insoluble in carbon tetrachloride or water and dissolved only slowly in acetone.

Reactions of Cinnamylamine (6). (a) With Allylmagnesium Chloride; Isolation of 7. A solution of **6** (1.50 g, 113 mmol) in THF (20 mL) was added to a commercial THF solution of allylmagnesium chloride (11 mL, 3.0 M, 33 mmol). The resulting solution was refluxed for 17 h, during which time a precipitate appeared, and then was worked up by using procedure A. The solvent was removed at reduced pressure and the remainder distilled to give **7**: 0.44 g (2.51 mmol, 23%); bp 78–79 °C (0.7 torr); IR (CCl_4) 3390 and 3300 (NH_2), 1640 (C=C), 1604 (NH_2) cm^{-1}; ^1H NMR (CCl_4) δ 1.00 (s, 2, disappears on shaking with D_2O, NH_2), 1.67 (m, 1, $CHCH_2N$), 2.06 (t, 2, J = 6 Hz, $=CHCH_2$), 2.53 (c, 4, NCH_2 and $PhCH_2$), 4.88 (m, 1, =CHH), 5.12 (m, 1, =CHH), 5.43–6.07 (m, 1, =CH), 7.16 (m, 5, Ph). The distillate was purified by GC (column A, 175 °C) to free it from a trace of **6**. Anal. Calcd for $C_{12}H_{17}N$: C, 82.23; H, 9.78; N, 7.99. Found: C, 82.28; H, 9.80; N, 7.78.

(b) With Allylmagnesium Chloride and 1-Phenyl-1-propene. A solution of **6** (1.00 g, 7.5 mmol) and 1-phenyl-1-propene (0.89 g, 7.5 mmol) in THF (25 mL) was added to a commercial THF solution of allylmagnesium chloride (10 mL, 3.0 M, 30 mmol). The resulting solution was refluxed for 15 h and then worked up by using procedure A. The solvent was removed at reduced pressure, leaving a liquid. GC analysis (column A, 155

(38) Shriner, R. L.; Fuson, R. C.; Curtin, D. Y. "The Systematic Identification of Organic Compounds", 5th ed.; Wiley: New York, 1964; p 261.
(39) Wedekind, E. *Chem. Ber.* **1909**, *42*, 3939.
(40) D'Arcy, R.; Grob, C. A.; Kaffenberger, T.; Krasnobajew, V. *Helv. Chim. Acta* **1966**, *49*, 185.
(41) This product has already been isolated from reactions of allylmagnesium chloride in THF: Richey, H. G., Jr.; Von Rein, F. W.; Szucs, S. S., unpublished observations. For a related product isolated from a solution of cinnamylmagnesium bromide in THF, see: Tanigawa, Y.; Moritani, I.; Nishida, S. *J. Organomet. Chem.* **1971**, *28*, 73.

°C, dodecane standard) showed a 65% recovery of 1-phenyl-1-propene, a 25% yield of 7 (relative retention times 1.0 and 5.1), and the absence of 6. Presumably, no product of addition to 1-phenyl-1-propene was present since no unidentified peak with retention time greater than that of 1-phenyl-1-propene was noted.

Reactions of 3-Amino-1-phenyl-1-propyne (8). (a) With Allylmagnesium Chloride; Formation of 9. A solution of 8 (0.50 g, 3.8 mmol) in THF (6 mL) was added to a commercial THF solution of allylmagnesium chloride (4 mL, 3.0 M, 12 mmol). The resulting solution was kept at ambient temperature for 21 h and then worked up by using procedure A. GC analysis (column D, 150 °C) of the liquid remaining after the solvent was removed at reduced pressure showed three peaks (relative retention times 1.0, 1.5, and 6.4). The compounds responsible for the first two peaks were shown to be 2-methyl-4-penten-1-ol and 6-hepten-1-ol by their retention times and by noting their absorptions in the IR and ^{1}H NMR spectra of the crude product (see reaction of allylamine with allylmagnesium chloride in THF for more about these alcohols). The third component was collected and shown by its IR and ^{1}H NMR spectra to be 8. The yield (hexadecane standard) of 8 was 40%.

In another reaction, a solution of 8 (2.00 g, 15 mmol) in THF (25 mL) was added to a commercial THF solution of allylmagnesium chloride (15 mL, 3.0 M, 45 mmol). The resulting solution was refluxed for 21 h before being worked up by use of procedure A. GC analysis (column D, 150 °C) of the liquid remaining after the solvent was removed at reduced pressure showed two peaks (88% and 12% of the total peak area; relative retention times 1.0 and 1.6). By the relative retention times and by noting the appropriate absorptions (and no others) in the IR and ^{1}H NMR spectra of the crude product, it was shown that the first peak was due both to 2-methyl-5-penten-1-ol and 9 and the second peak to 6-hepten-1-ol. The yield of 9 was calculated to be 44% by determining (hexadecane standard) the weight of material responsible for the first GC peak and the composition of that material by comparing areas of the ^{1}H NMR absorptions due to the phenyl hydrogens of 9 and the methyl hydrogens of 2-methyl-5-penten-1-ol.

(b) With Butylmagnesium Bromide; Formation of 9. THF (6 mL) was added to a commercial diethyl ether solution of butylmagnesium chloride (3.8 mL, 3.0 M, 11.4 mmol) in the reaction apparatus which was fitted with a 10-cm distillation column packed with glass helices. The solution was distilled until the head temperature reached 65 °C. Then a solution of 8 (0.50 g, 3.8 mmol) in THF (6 mL) was added to the remainder. The resulting solution was refluxed for 22 h and then worked up by using procedure A. GC analysis (column D, 130 °C) of the liquid (0.20 g) remaining after removing the solvent at reduced pressure gave two peaks (34% and 66% of the total peak area, relative retention times of 1.0 and 1.6). The compound responsible for the first peak was shown by its IR and ^{1}H NMR spectra to be 1-butanol. This compound probably formed as a result of exposure of the commercial Grignard reagent solution to oxygen. The compound responsible for the second peak was shown to be 9 by its retention time and by noting its absorptions (and no others except those of 1-butanol) in the IR and ^{1}H NMR spectra of the crude product.

Reaction of *N*-Allyl-*N*-methylaniline with Allylmagnesium Chloride. A solution of the amine (2.87 g, 19.5 mmol) was added to a Grignard reagent solution prepared from allyl chloride (6.18 g, 81 mmol) and magnesium (2.13 g, 88 mmol) in diethyl ether (70 mL). The suspension was refluxed for 48 h and then worked up by using procedure A. About 70% of the *N*-allyl-*N*-methylaniline was recovered upon distillation at reduced pressure. The distillate was shown by GC analysis (column F, 170 °C) to contain a small amount of *N*-methylaniline, but about the same amount was found to be present in the sample of *N*-allyl-*N*-methylaniline used for the reaction.

Reaction of *N,N*-Dimethylallylamine with Allylmagnesium Chloride. A solution of the amine (4.25 g, 50 mmol) in THF (50 mL) was added to a commercial THF solution of allylmagnesium chloride (33.3 mL, 3.0 M, 100 mmol). The solution was refluxed for 8 h and worked up by using procedure B. The organic layer was extracted with a 5% hydrochloric acid solution. The resulting aqueous layer was made basic with a 5% sodium hydroxide solution and extracted with diethyl ether. The ether solution was dried ($MgSO_4$) and distilled to remove most of the diethyl ether. The ^{1}H NMR spectrum of the remainder showed the presence only of some THF.

Reactions of *N,N*-Diethylallylamine with Allylmagnesium Chloride. A solution of the amine (5.65 g, 50 mmol) in THF (50 mL) was added to a commercial THF solution of allylmagnesium chloride (33.3 mL, 3.0 M, 100 mmol). The solution was refluxed for 8 h and worked up by using procedure B. After removal of most of the solvent, GC analysis (column B) showed the presence of *N,N*-diethylallylamine. A minor peak with a longer retention time was shown by a ^{1}H NMR spectrum to be due to 6-hepten-1-ol.

By use of a procedure similar to that reported[42] for the preparation of some Grignard reagents in benzene containing triethylamine, allylmagnesium chloride was prepared in toluene containing *N,N*-diethylallylamine. Methyl iodide (~1 mL) was added to magnesium (2.3 g, 95 mmol) followed by a solution of the amine (8.0 g, 71 mmol) and toluene (6 mL). After several minutes, the solution became cloudy. The mixture was then stirred and heated at 40–50 °C while a solution of allyl chloride (5.4 g, 71 mmol) in toluene (80 mL) was added over 3 h. A large amount of fluffy white precipitate was present, and most of the magnesium had disappeared. Without the use of methyl iodide, no reaction was observed. Then more toluene (40 mL) was added, and the mixture was refluxed for 18 h. After a workup using procedure B, the organic solution was extracted with 5% hydrochloric acid. The aqueous extract was made basic with a 5% sodium hydroxide solution and then extracted with diethyl ether. After the extracts were dried ($MgSO_4$) and most of the solvent was removed, distillation at reduced pressure gave two fractions. The first fraction [4.6 g; bp 10–11 °C (1 torr)] was shown by its ^{1}H NMR spectrum to be *N,N*-diethylallylamine. The second fraction [0.8 g; bp 18–21 °C (1 torr)] was shown by its ^{1}H NMR spectrum to contain about 50% *N,N*-diethylallylamine. Other absorptions were present, but not those that would be expected for $>NCH_2$ or $CH_2CH=$ of an addition product. The recovery of the amine was about 62%.

Reactions of *N,N*-Dimethylcinnamylamine (10). (a) With Allylmagnesium Chloride; Isolation of 11. A commercial THF solution of allylmagnesium chloride (24.8 mL, 3.0 M, 74.4 mmol) was added to the reaction apparatus equipped with a take-off condenser, and THF (12.5 mL) was removed by distillation. The solution was cooled, and 10 (4.00 g, 24.8 mmol) in toluene (20 mL) was added. After the addition, heating was resumed and distillation continued until a head temperature of 70 °C was reached (4.5 mL of distillate was collected). More toluene (30 mL) was added and the reaction mixture refluxed for 40 h. The resulting solution was hydrolyzed with water (15 mL). The resulting mixture was filtered and the filtrate extracted with three 25-mL portions of a 5% hydrochloric acid solution. The acid extracts were made basic with a 5% sodium hydroxide solution and extracted with diethyl ether. The ether extracts were dried ($MgSO_4$), and then most of the solvent was removed. Distillation of the residue at reduced pressure gave two fractions (1.2 and 1.0 g) which proved to be 11: 10.8 mmol (44%); bp (fraction 1) 92–95 °C (2.2 torr), bp (fraction 2) 101–121 °C (2.8 torr); IR (CCl_4) 1645 cm^{-1} (C=C); ^{1}H NMR (CCl_4) δ ~2.0 (c, 5, $CHCH_2CH=$ and CH_2Ph or $=CH_2N$), 2.11 (s, 6, CH_3), 2.60 (m, 2, CH_2Ph or CH_2N), 4.95 (m, 1, =CHH), 4.98 (m, 1, =CHH), ~5.7 (m, 1, =CH), 7.15 (m, 5, Ph); ^{1}H NMR (CF_3CO_2H) 2.25 (c, 3, $CHCH_2N$ and CH_2Ph or $CH_2CH=$), ~2.7 (m, 2, CH_2Ph or $CH_2CH=$), 2.79 (d, 3, J = 5 Hz, CH_3NCH_3), 2.87 (d, 3, J = 5 Hz, CH_3NCH_3), 3.13 (m, 2, CH_2N), 5.20 (m, 1, =CHH), 5.25 (m, 1, =CHH), ~5.8 (m, 1, =CH), 7.33 (m, 5, Ph); mass spectrum, m/z 203.1638 (M^+, calcd for $C_{14}H_{21}N$ 203.1673). A sample was purified by GC (column B) for analysis. Anal. Calcd for $C_{14}H_{21}N$: C, 82.70; H, 10.41; N, 6.89. Found: C, 82.45; H, 10.55; N, 6.72. A low-resolution mass spectrum of the second distillation fraction contained peaks at m/z 245 and 287 as well as at m/z 203. GC analysis of the second fraction (column B) revealed, in addition to the major peak for 11 (retention time 2.8 relative to that of 10), a minor peak for 10 and two minor peaks (retention times of 12.0 and 15.8) which may have been due to products resulting from further addition

(42) Ashby, E. C.; Reed, R. *J. Org. Chem.* **1966**, *31*, 971.

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, =C**H**CH_2), 6.50 (br s, 1, =C**H**Ph), 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.

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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.

(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

(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.

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