Transformation of Carbon–Oxygen into Carbon–Carbon Bonds Mediated by Low-Valent Nickel Species[1]

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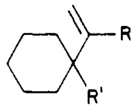
The substitution of alkoxy groups of enol ethers (1-methoxycyclohexenes, 1-methoxy-1-alkenes, and benzofuran) and aryl ethers (methoxynaphthalenes, cresyl methyl ethers, and dimethoxybenzenes) by hydrogen, alkyl groups, and aryl units, through Grignard reactions catalyzed by bis(triphenylphosphine)nickel dichloride or [1,3-bis(diphenylphosphino)propane]nickel dichloride, is described. The stereochemistry of the new reaction is portrayed, especially in connection with processes involving ring opening of dihydropyrans and dihydrofurans. The reaction has been applied to the synthesis of a termite trail pheromone and the acetate of the Douglas fir beetle aggregation pheromone.

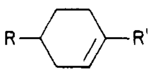
The reaction between Grignard reagents and allyl alcohols in the presence of phosphine-ligated nickel salts in benzene solution, causing the replacement of the hydroxy group by hydrogen or an alkyl group, has been known for some time[2] and has found application in natural products synthesis.[3] In continuation of the latter study it became of interest to investigate the behavior of allyl alcohols with heteroatom substituents toward Grignard reagents.[4,5] As one example of such reactions the chemistry of a 2-methoxy-2-propen-1-ol was inspected and 1-(α-methoxyvinyl)-1-cyclohexanol (**1a**)[6] chosen as starting material.



1a, R = OMe, R' = OH
b, R = Me, R' = OH
c, R = Me, R' = C_6H_5
d, R = R' = C_6H_5

Interaction of methylmagnesium bromide and bis(triphenylphosphine)nickel dichloride [$(tpp)_2NiCl_2$] with alcohol **1a** yielded product **1b**. Whereas the absence of allyl alcohol activity could be attributed to the rate-retarding effect of the substituents of the sterically quite encumbered starting compound,[2] the replacement of the methoxy group was unprecedented and appeared mechanistically unrelated to the reactions of allyl alcohols. The inertness of the product **1b** to the Grignard reagent on its resubmission to the reaction conditions from which it had been created indicated that the reaction outcome was not the result of early quenching of the reaction and reconfirmed the importance of steric factors in the allyl alcohol reaction. Contrastingly, the more powerful Grignard reagent phenylmagnesium bromide[5] underwent a reaction with alcohol **1b** (methylmagnesium bromide having served first as a base toward the alcohol and as a reducing agent toward $(ttp)_2NiCl_2$), yielding olefin **1c**. Furthermore, the reaction of phenylmagnesium bromide with allyl alcohol **1a** led to fully deoxygenated olefin **1d**. The unusual behavior of the starting material **1a** suggested that a new reaction had been uncovered. As a consequence the following study of enol ethers with Grignard reagents in the presence of low-valent nickel species was undertaken.

Exposure of methylmagnesium bromide to enol ether **2a** under the influence of the nickel catalyst yielded cyclohexene **2d** and the reactions of phenylmagnesium bromide with ethers **2a** and **2b** gave olefins **2e** and **2f**, respectively. Reactions of the latter Grignard reagent with the silyl enol ether **2c** afforded product **2f**, albeit in low yield,[7] while the same reagent converted phenyl vinyl ether into styrene and phenol. Its interaction with the methyl enol ether of 2,6-dimethylcyclohexanone and the enol acetates of acetone and cyclohexanone failed, indicative of the low reactivity of highly substituted enol ethers as well as magnesium enolates.[8,9]



2a, R = *t*-Bu, R' = OMe
b, R = H, R' = OMe
c, R = H, R' = $OSiMe_3$
d, R = *t*-Bu, R' = Me
e, R = *t*-Bu, R' = C_6H_5
f, R = H, R' = C_6H_5

The next reactions were based on (*E*)-1-methoxydecene (**3a**)[10] as starting enol ether and [1,3-bis(diphenylphosphino)propane]nickel dichloride ($dpppNiCl_2$) as catalyst, the latter being used in place of $(tpp)_2NiCl_2$ in view of it leading to higher yields of olefinic products (vide infra).[1] Reactions with phenylmagnesium, methylmagnesium, and ethylmagnesium bromides gave olefins **3b–d** in 84, 77, and 50% yields, respectively. Whereas the last Grignard reagent might have been expected to act both as an alkyl group transfer agent and as a reducing agent, it showed no reducing properties in the presence of a chelating ligand around the metal. However, the better reducing agent, isopropylmagnesium bromide, in the presence of the ligand-releasing catalyst $(tpp)_2NiCl_2$ afforded the reduction product **3e** accompanied by the alkylation product **3f**[11] in ca. 2:1 ratio (51% total yield).[12]

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* To whom correspondence should be addressed at the University of California—San Diego.

[1] For a preliminary communication see: Wenkert, E.; Michelotti, E. L; Swindell, C. S. *J. Am. Chem. Soc.* **1979**, *101*, 2246.

[2] Felkin, H.; Swierczewski, G. *Tetrahedron* **1975**, *31*, 2735.

[3] Buckwalter, B. L.; Burfitt, I. R.; Felkin, H.; Joly-Goudket, M.; Naemura, K.; Salomon, M. F.; Wenkert, E.; Wovkulich, P. M. *J. Am. Chem. Soc.* **1978**, *100*, 6445.

[4] For the reaction of α,β-unsaturated acetals, i.e., allyl alcohol derivatives with C(1) heteroatom substituents, see: Wenkert, E.; Ferreira, T. W. *Organometallics* **1982**, *1*, 1670.

[5] Swindell, C. S. Ph.D. Dissertation, Rice University, 1979. Wenkert, E. *Chimia* **1981**, *35*, 257.

[6] Baldwin, J. E.; Höfle, G. A.; Lever, O. W., Jr. *J. Am. Chem. Soc.* **1974**, *96*, 7125.

[7] For the reactions under the influence of bis(acetylacetonato)nickel affording higher product yields see: Hayashi, T.; Katsuro, Y.; Kumada, M. *Tetrahedron Lett.* **1980**, 3915.

[8] On the other hand, dienolates undergo the reaction. Thus the reaction of the lithium enolate of crotonaldehyde with phenylmagnesium bromide led to 1-phenyl-1,3-butadiene (in low yield), as did the reaction of 1-methoxy-1,3-butadiene (in 72% yield).

[9] In contrast to enol ethers the reactions of enamines, e.g., the reaction of phenylmagnesium bromide with the pyrrolidine enamine of cyclohexanone, failed.

[10] De Simone, R. S. (Hercules, Inc.), U.S. Patent 4 280 011 (*Chem. Abstr.* **1981**, *95*, 219 773).

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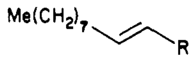
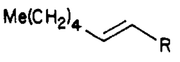
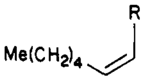


3a, R = OMe
b, R = C_6H_5
c, R = Me
d, R = Et
e, R = H
f, R = $(CH_2)_2Me$



4a-c

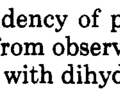


5a-c

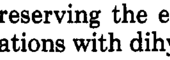
a, R = OMe
b, R = C_6H_5
c, R = Me

When a 1.3:1 mixture of (*E*)- (**4a**) and (*Z*)-1-methoxyheptenes (**5a**)[13] was exposed to phenylmagnesium and methylmagnesium bromides in the presence of $(tpp)_2NiCl_2$, a 1.7:1 mixture of styrenes **4b** and **5b** (79% total yield) and a 1.4:1 mixture of 2-octenes **4c** and **5c** (70% total yield), respectively, were obtained. These observations gave the first clue regarding the stereochemistry of the reaction, revealing preponderance of retention of configuration with a small tendency for a cis-to-trans inversion.

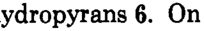
An illustration of the efficacy of the new reaction and its tendency of preserving the enol ether configuration came from observations with dihydropyrans **6**. On interaction with dihydropyran (**6a**) (followed by product acetylation) methylmagnesium bromide in the presence of $(tpp)_2NiCl_2$ yielded a ca. 3:1 mixture of olefins **7a** and **8a**, the former being the sole product in the presence of $dpppNiCl_2$. Reactions with phenylmagnesium bromide converted dihydropyran (**6a**) into olefin **7b** under the influence of $(tpp)_2NiCl_2$ and into a ca. 20:1 mixture of olefins **7b** and **8b** in the presence of $dpppNiCl_2$. A reaction of 2-ethyldihydropyran (**6b**) with methylmagnesium bromide and $dpppNiCl_2$ and subsequent acetylation gave olefin **9**. Thus, once again, high preponderance of retention of configuration had been maintained. The reactions of dihydropyran (**6a**) with ethylmagnesium bromide (followed by product acetylation) led to ethylation and reduction products, the former having maintained a cis-olefin configuration. Catalysts $(tpp)_2NiCl_2$ and $dpppNiCl_2$ guided the reaction to compounds **7c** and **7d** in ca. 1.5:1 and 5:1 ratios, respectively. The most efficient procedure for the reduction of dihydropyran (**6a**), i.e., for the exclusive formation of olefin **7d**, involved the use of isopropylmagnesium bromide and $(tpp)_2NiCl_2$ or cyclohexylmagnesium bromide and a 1:1 mixture of $NiCl_2$ and tpp.[14]



6a, R = H
b, R = Et

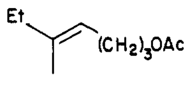


7a-d



8a-d

a, R = Me, R' = Ac
b, R = C_6H_5, R' = H
c, R = Et, R' = Ac
d, R = H, R' = Ac



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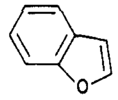
The next enol ether type to come under scrutiny was the furanoid system, of which benzofuran (**10**) became the first example. Whereas the aromatic bicycle was stable at room temperature, the furan moiety became vulnerable in refluxing benzene and underwent ring opening. In the presence of $(tpp)_2NiCl_2$ catalyst the reactions with methylmagnesium and phenylmagnesium bromides gave approximately a 4:1 *o*-(*Z*)- (**11a**) and *o*-(*E*)-propenylphenol (**11b**) mixture and *o*-hydroxy-(*E*)-stilbene (**11c**), respectively. Presumably, the *cis*-stilbene had undergone isomerization into the more stable trans product in the reaction medium. On use of $dpppNiCl_2$ as catalyst the two reactions led to a ca. 1:2 **11a**–**11b** mixture and **11c**, respectively. Thus the catalyst ligand had affected the stereochemical outcome of the reaction. Whereas the accumulated data were insufficient to preclude the possibility of the trans products being, at least in part, primary reaction products, $dpppNiCl_2$ could be shown to be responsible for cis–trans isomerization. Thus exposure of styrene **11a** to this catalyst and methylmagnesium bromide under reaction conditions similar to those used in the formation of **11a** led to approximately a 1:3 mixture of styrenes **11a** and **b**, respectively. Finally, it was noteworthy that in none of the reactions with benzofuran (**10**) the benzene ring was deoxygenated.



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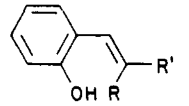

11a, R = Me, R' = H
b, R = H, R' = Me
c, R = H, R' = C_6H_5

In continuation of the study of the Grignard reactions of furanoid systems an investigation of the chemistry of dihydrofuran (**12a**) and 2-methyldihydrofuran (**12b**) was undertaken. This study was considered especially important, since the anticipated 3-buten-1-ol products (**13** and **14**) could be expected to be of use in the fields of pheromone and terpene synthesis. The first enol ether proved to be so reactive as to require the reactions to be executed at 0–5 °C by the slow, continuous addition of the ether to a mixture of the Grignard reagent and the catalyst. In the presence of $(tpp)_2NiCl_2$ the reaction between dihydrofuran (**12a**) and methylmagnesium bromide gave (after acetylation) approximately a 5:1 mixture of olefins **13a** and **14a** and the reaction with phenylmagnesium bromide yielded olefin **13b**. However, the use of $dpppNiCl_2$ as catalyst led to a ca. 1:1 mixture of olefins **13a** and **14a** and a ca. 1:2 mixture of olefins **13b** and **14b**, respectively. Thus, as in the case with benzofuran (**10**), the stereochemical course of the reaction showed a strong dependence on the nature of the catalyst ligand, chelation of the metal by dppp showing a trend toward inversion of olefin configuration. The fact of *cis*-styrene **13b** yielding a 3:2 **13b**–**14b** mixture on treatment with phenylmagnesium bromide and $dpppNiCl_2$ under conditions identical with those of the compound's production in a 1:2 **13b**–**14b** mixture from dihydrofuran (**12a**) revealed that the unusual double-bond inversion had occurred both in the initial dihydrofuran unraveling and by a subsequent product isomerization. It is noteworthy that the formation of 4-phenyl-(*Z*)-3-buten-1-ol (**13b**) constitutes a one-step synthesis of the termite trail pheromone[15] and that of compound **14a** a synthesis of the acetate of the Douglas fir beetle aggregation pheromone.[16]

The chemistry of 2-methyldihydrofuran (**12b**) led to surprises, except for the $dpppNiCl_2$-mediated reaction with methylmagnesium bromide yielding (after acetylation) olefin **15a** and the $(tppp)_2NiCl_2$-induced reaction with

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[11] The nickel-mediated *n*-propyl group transfer with isopropylmagnesium salts has precedents: Tamao, K.; Kiso, Y.; Sumitani, K.; Kumada, M. *J. Am. Chem. Soc.* **1972**, *94*, 9268. Kiso, Y.; Tamao, K.; Kumada, M. *J. Organomet. Chem.* **1973**, *50*, C12.

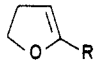
[12] The reaction with cyclohexylmagnesium bromide and $(tpp)_2NiCl_2$ led also to a ca. 2:1 mixture of reduction and substitution products **3e** and **3** (R = c-Hex), respectively.

[13] Rojas, A. C.; Crandall, J. K. *J. Org. Chem.* **1975**, *40*, 2225.

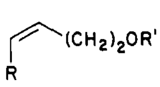
[14] Wenkert, E.; Ferreira, T. W. *J. Chem. Soc., Chem. Commun.* **1982**, 840.

[15] Zhong, C.-M.; Wang, P.-C.; Li, T.-H.; Liu, Y. C.; Kuang, D.-Z.; Liu, F.-P. *Lin Yeh K'o Hsueh* **1979**, *15*, 15 (*Chem. Abstr.* **1979**, *91*, 39041).

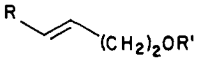
[16] Ryker, L. C.; Libbey, L. M.; Rudinsky, J. A. *Environ. Entomol.* **1979**, *8*, 789.



12a, R = H
b, R = Me



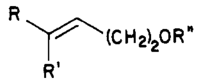
13a,b



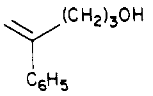
14a,b

a, R = Me, R' = Ac
b, R = C_6H_5, R' = H

isopropylmagnesium bromide furnishing (after acetylation) approximately a 20:1 reduction product mixture of **14a** and **13a**. With $(tpp)_2NiCl_2$ catalyst the reaction of phenylmagnesium bromide produced a 4:1 mixture of the product **15b** with retention of configuration and its unexpected isomer **16**, while under $dpppNiCl_2$ catalysis the reaction led to olefins **15b**, **15c**, and **16** in ca. 6:3:1 ratio. Thus, once more, $dpppNiCl_2$ tended to drive the reaction toward products with inverted configuration. All phenylated compounds appeared to be primary products, as indicated by the lack of effect of changes in the reaction time and temperature on the product ratio. The reaction of ethylmagnesium bromide under the influence of $(tpp)_2NiCl_2$ led exclusively (after acetylation) to the reduction products **14a** and **13a** in 7:1 ratio. However, in the presence of $dpppNiCl_2$ both ethylation and reduction products were obtained—compounds **15d**, **15e**, **14a**, and **13a** in 24:8:7:1 ratio. Perhaps the most interesting result in the experiments with 2-methyldihydrofuran (**12b**) was the formation of the reduction product **13a**. Since this compound was the product of inversion of configuration and simultaneously a product of thermodynamically unstable configuration, its formation represents a clear indication of the inversion process not being a trivial post-equilibration step but representing a phenomenon requiring explanation as part of the mechanism of the carbon–oxygen to carbon–carbon bond transformation.



15a, R = R' = Me, R'' = Ac
b, R = Me, R' = C_6H_5, R'' = H
c, R = C_6H_5, R' = Me, R'' = H
d, R = Me, R' = Et, R'' = Ac
e, R = Et, R' = Me, R'' = Ac



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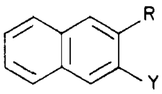
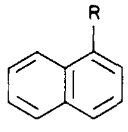
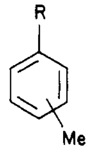


17a, R = OMe, Y = H
b, R = $OSO_2C_6H_4Me$, Y = H
c, R = OH, Y = H
d, R = Y = OMe
e, R = Me, Y = H
f, R = C_6H_5, Y = H
g, R = Y = C_6H_5

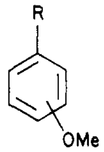
In the face of the ease of substitution of alkoxy groups of enol ethers by hydrogen and alkyl and aryl groups it was of interest to test the reactivity of another group of alkoxy-substituted, sp^2-hybridized substances, i.e., aryl ethers.[17] Hence a variety of anisoles were exposed to Grignard reagents under $(tpp)_2NiCl_2$ catalysis. The substitution process proceeded well in the case of aryl group transfer, especially in the naphthalene series, but not for alkyl group transfer, except for the conversion of β-methoxynaphthalene (**17a**) into β-methylnaphthalene (**17e**) by methylmagnesium bromide and $dpppNiCl_2$ catalyst in refluxing benzene or toluene. Phenylmagnesium bromide in the presence of $(tpp)_2NiCl_2$ catalyst transformed ether **17a**, β-naphthyl *p*-toluenesulfonate (**17b**), and even β-naphthol (**17c**) (albeit in low yield) into β-phenylnaphthalene (**17f**) and despite steric hindrance 2,3-dimethoxynaphthalene (**17d**) and α-methoxynaphthalene (**18a**) into 2,3-diphenylnaphthalene (**17g**) and α-phenylnaphthalene (**18b**), respectively. The reactions with phenyl ethers were of lower yield and exhibited strong steric effects. Thus *p*-cresyl ether (**19a**) and the meta isomer (**19b**) were converted into *p*- (**19d**) and *m*-methylbiphenyl (**19e**), respectively, while the ortho isomer (**19c**) remained unreacted. Similarly, hydroquinone dimethyl ether (**20a**) was changed into *p*-methoxybiphenyl (**20d**) and *p*-terphenyl (**21**), the former product being convertible into the latter in a separate reaction, resorcinol dimethyl ether (**20b**) was transformed into *m*-methoxybiphenyl (**20e**), and catechol dimethyl ether (**20c**) was left unchanged. More work will have to be expended to improve the aryl ether substitution reactions.



18a, R = OMe
b, R = C_6H_5

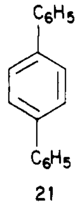


19a–e



20a–e

a, R = *p*-OMe
b, R = *m*-OMe
c, R = *o*-OMe
d, R = *p*-C_6H_5
e, R = *m*-C_6H_5



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Experimental Section

Melting points were taken on a Reichert micro hotstage and are uncorrected. Infrared spectra on films of liquids and KBr pellets of solids were measured on Beckman IR 4230 and Perkin-Elmer 457 spectrophotometers. ^1H NMR spectra were recorded on Varian EM-390 and XL-100-15 spectrometers and on a 360-MHz instrument with a highly modified Varian HR220 console, an Oxford magnet, and a Nicolet 1180-E computer system. ^{13}C NMR spectra of $CDCl_3$ solutions were taken on the Varian XL-100-15 instrument and a Nicolet NT-200 (wide-bore, broad-band, with Oxford magnet) spectrometer, operating at 25.02 and 50.31 MHz in the Fourier transform mode, respectively. The carbon shifts are in parts per million downfield from Me_4Si; $\delta(Me_4Si) = \delta(CDCl_3) + 76.9$ ppm. Low-resolution mass spectra were determined at 70 eV on a Finnigan 3300 GC–MS spectrometer and high-resolution mass spectra on a CEC 21-11013 spectrometer. Analytical gas chromatography was performed on Varian 1200 and 1400 flame ionization instruments, equipped with 3 ft × $^1/_8$ in. 10% OV 101 on Chromosorb W (80–100 mesh) columns.

1-Isopropenyl-1-cyclohexanol (1b). A 2.95 M ethereal solution of methylmagnesium bromide, 18 mL (53.1 mmol), was added to a stirring suspension of 654 mg (1.00 mmol) of $(tpp)_2NiCl_2$ in 30 mL of dry benzene under argon and the stirring continued at room temperature for 15 min. A solution of 1.56 g (10.0 mmol) of 1-(α-methoxyvinyl)-1-cyclohexanol (**1a**)[6] in 2 mL of dry benzene was added dropwise, most of the ether removed by distillation, and the mixture refluxed for 44 h. It then was acidified with 1 N hydrochloric acid and extracted with methylene chloride. The extract was dried (Na_2SO_4) and evaporated. Distillation (80–90 °C/10 torr) of the residue yielded 1.01 g (72%) of alcohol **1b**:[18] IR OH 3440 (s), C=C 1640 (m) cm^{-1}; ^1H NMR (CCl_4) δ 0.8–2.3 (m, 10, methylenes), 1.53 (s, 3, Me), 4.6–4.9 (m, 2, olefinic Hs); MS, *m/e* (relative intensity) 140 (M^+, 3), 109 (37), 108 (30), 97 (93), 96 (93), 69 (57), 68 (40), 55 (50), 54 (40), 43 (97), 42 (93), 41 (base), 40 (90).

Subjection of the product to a reaction identical to that from which it was derived led only to its recovery.

1-Isopropenyl-1-phenylcyclohexane (1c). A 2.5 M ethereal solution of methylmagnesium bromide, 2.5 mL (6.3 mmol), was added to a stirring suspension of 327 mg (0.50 mmol) of $(tpp)_2$-

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[17] For nickel-catalyzed reactions of aryl phosphates with Grignard reagents see: Hayashi, T.; Katsuro, Y.; Okamoto, Y.; Kumada, M. *Tetrahedron Lett.* 1981, 4449.

[18] Bhalerao, U. T.; Rapoport, H. *J. Am. Chem. Soc.* 1971, *93*, 4835.

NiCl$_2$ in 15 mL of dry benzene under argon and the stirring continued at room temperature for 15 min. A solution of 700 mg (5.0 mmol) of alcohol **1b** in 2 mL of dry benzene was added dropwise. Thereafter 6.8 mL (15.0 mmol) of a 2.2 M ethereal solution of phenylmagnesium bromide was added, most of the ether removed by distillation and replaced by 14 mL of dry benzene, and the mixture refluxed for 24 h. It then was poured into a saturated ammonium chloride solution and extracted with hexane. The extract was dried (MgSO$_4$), filtered through basic alumina, and evaporated. Chromatography of the residue on 50 g of silica impregnated with 15% silver nitrate, and elution with hexane furnished 603 mg (63%) of liquid olefin **1c**: IR C═C 1640 (w), 1605 (w), 1500 (m), 1455 (m) cm^{-1}; ^{1}H NMR (CCl$_4$) δ 1.2–2.3 (m, 10, methylenes), 1.43 (s, 3, Me), 4.8–5.0 (m, 2, olefinic Hs), 6.9–7.4 (m, 5, aromatic Hs); ^{13}C NMR δ 19.9 (Me), 22.7 (C-3, C-5), 26.4 (C-4), 35.0 (C-2, C-6), 47.2 (C-1), 110.9 (olefinic CH$_2$), 125.3 (para C), 126.6 (2 ortho C), 127.7 (2 meta C), 146.7 (ipso C), 150.1 (olefinic C); MS, *m/e* (relative intensity) 200 (M$^+$, 17), 143 (29), 129 (47), 128 (21), 118 (40), 117 (28), 115 (27), 91 (base), 81 (20), 77 (23), 55 (20), 51 (20), 41 (47); exact mass, *m/e* 200.1570 (calcd for C$_{15}$H$_{20}$, *m/e* 200.1565).

1-Phenyl-1-α-styrylcyclohexane (1d). A 2.95 M ethereal solution of methylmagnesium bromide, 2.0 mL (5.9 mmol), was added to a stirring suspension of 327 mg (0.50 mmol) of (tpp)$_2$NiCl$_2$ in 15 mL of dry benzene under argon and the stirring continued at room temperature for 15 min. A solution of 780 mg (5.0 mmol) of alcohol **1a** in 2 mL of dry benzene was added dropwise. Thereupon 10.8 mL (15.1 mmol) of a 1.4 M ethereal solution of phenylmagnesium bromide was added, most of the ether distilled off and replaced by 13 mL of dry benzene, and the mixture refluxed for 27 h. Workup and product chromatography as above yielded 600 mg (46%) of liquid olefin **1d** (Kugelrohr distilled at 120–125 °C/0.05 torr): IR C═C 1620 (w), 1600 (w), 1490 (m), 1450 (s) cm^{-1}; ^{1}H NMR (CCl$_4$) δ 1.0–2.3 (m, 10, methylenes), 5.15, 5.17 (d, 1 each, *J* = 16 Hz, olefinic Hs), 6.4–7.5 (m, 10, aromatic Hs); ^{13}C NMR δ 22.6 (C-3, C-5), 26.2 (C-4), 35.8 (C-2, C-6), 47.1 (C-1), 115.4 (olefinic CH$_2$), 125.6 (1-phenyl para C), 126.3 (2 1-phenyl ortho C), 127.9 (2 1-phenyl meta C), 142.6 (1-phenyl ipso C), 155.0 (olefinic C); MS, *m/e* (relative intensity) 262 (M$^+$, 7), 159 (33), 91 (base), 90 (53), 81 (27). Anal. (C$_{20}$H$_{22}$) C, H.

General Procedure for the Reactions of Enol Ethers with Grignard Reagents. A 2.9 M ethereal solution of methylmagnesium bromide, 0.8 mL (2.0 mmol), was added to a stirring suspension of 1.0 mmol of catalyst, (tpp)$_2$NiCl$_2$ or dpppNiCl$_2$ or 1:1 tpp–NiCl$_2$,[14] in 15 mL of dry benzene under argon and the stirring continued at room temperature for 15 min. At the end of this catalyst reduction the proper Grignard reagent, 10.0 mmol, was added and most of the ether removed by distillation and replaced by 10 mL of dry benzene. The enol ether, 10.0 mmol, was added and the solution refluxed under argon for 20 h. The cooled reaction mixture was poured into a saturated ammonium chloride solution and extracted with ether. The extract was dried (Na$_2$SO$_4$) and evaporated. The residue was chromatographed on silica gel impregnated with 15% silver nitrate (in the cases of nonpolar olefinic products) or on silica gel alone (in the cases of the olefinic alcohols or acetates) and eluted with hexane, hexane–ether mixtures, and ether.

4-*tert*-Butyl-1-methylcyclohexene (2d), prepared from 4-*tert*-butyl-1-methoxycyclohexene (**2a**),[19] methylmagnesium bromide, and (tpp)$_2$NiCl$_2$: liquid (59%), spectrally identical with an authentic sample.[20]

4-*tert*-Butyl-1-phenylcyclohexene (2e), prepared from **2a**, phenylmagnesium bromide, and (tpp)$_2$NiCl$_2$: liquid (75%), spectrally the same as an authentic material.[21]

1-Phenylcyclohexene (2f), prepared from 1-methoxycyclohexene (**2b**),[13,22] phenylmagnesium bromide, and (tpp)$_2$NiCl$_2$: liquid (71%), spectrally identical with an authentic specimen;[23] prepared from 1-((trimethylsilyl)oxy)cyclohexene (**2c**)[24] and same reagent and catalyst—35%.

Styrene and phenol, prepared from phenyl vinyl ether,[25] phenylmagnesium bromide, and (tpp)$_2$NiCl$_2$: GC identification and yield; styrene (93%) and phenol (62%).

1-Phenyl-(*E*)-1-decene (3b), obtained from a reaction of 1-methoxy-(*E*)-1-decene (**3a**)[10] [prepared from 1-decyne by the method of Kumada[26] in 20% yield: IR C═C 1650 (m) cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 0.82 (t, 3, *J* = 7 Hz, Me), 1.0–1.4 (s, 12, methylenes), 1.6–2.0 (m, 2, allyl H$_2$), 3.50 (s, 3, OMe), 4.70 (dt, 1, *J* = 14, 7 Hz, H-2), 6.28 (d, 1, *J* = 14 Hz, H-1); ^{13}C NMR δ 14.0 (C-10), 22.6 (C-9), 27.6 (C-3), 29.0, 29.2, 29.4 (C-5 to C-7), 30.7 (C-4), 31.8 (C-8), 55.7 (OMe), 103.1 (C-2), 146.7 (C-1)], phenylmagnesium bromide, and dpppNiCl$_2$: liquid (84%);[27] IR C═C 1590 (w), 1490 (w), 1450 (w) cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 0.90 (t, 3, *J* = 7 Hz, Me), 1.0–1.6 (m, 12, methylenes), 2.19 (q, 2, *J* = 7 Hz, allyl H$_2$), 6.10 (dt, 1, *J* = 16, 7 Hz, H-2), 6.28 (d, 1, *J* = 16 Hz, H-1), 7.0–7.2 (m, 5, aromatic Hs); ^{13}C NMR δ 14.0 (C-10), 22.6 (C-9), 29.2, 29.2, 29.3, 29.4 (C-4 to C-7), 31.8 (C-8), 33.0 (C-3), 125.8 (ortho C), 126.6 (para C), 128.3 (meta C), 129.5 (C-1), 131.1 (C-2), 137.8 (ipso C).

(*E*)-2-Undecene (3c), prepared from **3a**, methylmagnesium bromide and dpppNiCl$_2$: liquid (77%);[28] IR C═C 1620 (w) cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 0.88 (t, 3, *J* = 7 Hz, Me), 1.1–1.4 (m, 12, methylenes), 1.62 (d, 3, *J* = 4 Hz, olefinic Me), 1.7–2.2 (m, 2, allyl Hs), 5.3–5.5 (m, 2, olefinic Hs); ^{13}C NMR δ 14.0 (C-11), 17.8 (C-1), 22.6 (C-10), 29.2, 29.3, 29.5, 29.6 (C-5 to C-8), 31.9 (C-9), 32.6 (C-4), 124.4 (C-2), 131.6 (C-3).

(*E*)-3-Dodecene (3d), prepared from **3a**, ethylmagnesium bromide, and dpppNiCl$_2$: liquid (50%);[29] IR C═C 1620 (w) cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 0.86, 0.92 (t, 3 each, *J* = 7 Hz, methyls), 1.1–1.6 (m, 12, methylenes), 1.8–2.2 (m, 4, allyl Hs), 5.3–5.5 (m, 2, olefinic Hs); ^{13}C NMR δ 13.9 (C-1 or C-12), 14.0 (C-12 or C-1), 22.6 (C-11), 25.5 (C-2), 29.1, 29.2, 29.4, 29.6 (C-6 to C-9), 31.8 (C-10), 32.5 (C-5), 129.3 (C-3), 131.7 (C-4).

1-Decene (3e) and (*E*)-4-tridecene (3f), prepared from **3a**, isopropylmagnesium bromide and (tpp)$_2$NiCl$_2$: liquid olefin **3e** (34%), identical with commercially available product. Liquid olefin **3f** (17%):[30] ^{1}H NMR (CCl$_4$) δ 0.89 (t, 6, *J* = 7 Hz, methyls), 1.2–1.4 (m, 14, methylenes), 1.9–2.0 (m, 4, allyl Hs), 5.3–5.4 (m, 2, olefinic Hs); ^{13}C NMR δ 13.6 (C-1), 14.0 (C-13), 22.6 (C-12), 22.7 (C-2), 29.1, 29.2, 29.4, 29.6 (C-7 to C-10), 31.8 (C-11), 32.5 (C-6), 34.6 (C-3), 129.9 (C-4 or C-5), 130.5 (C-5 or C-4).

1-Phenyl-1-heptenes (4b and 5b), prepared from a 1.3:1 **4a–5a** mixture, phenylmagnesium bromide, and (tpp)$_2$NiCl$_2$: liquid olefin mixture (79%);[31] ^{1}H NMR (CCl$_4$) δ 0.7–1.1 (m, 3, Me), 1.1–1.7 (m, 6, methylenes), 2.0–2.4 (m, 2, allyl Hs), 5.4–6.5 (m, 2, olefinic Hs), 6.9–7.4 (m, 5, aromatic Hs). **4b** (63% of mixture): ^{13}C NMR δ 14.0 (C-7), 22.6 (C-6), 29.0 (C-4), 31.4 (C-5), 33.0 (C-3), 125.7 (ortho C), 126.5 (para C), 128.2 (meta C), 129.5 (C-2), 130.9 (C-1), 137.7 (ipso C). **5b** (37% of mixture): ^{13}C NMR δ 14.0 (C-7), 22.6 (C-6), 28.6 (C-3), 29.7 (C-4), 31.4 (C-5), 126.2 (para C), 127.9 (ortho C), 128.5 (meta C), 128.5 (C-1), 133.0 (C-2), 137.6 (ipso C). Heating of the olefin mixture and a catalytic quantity of thiophenol and azobis(isobutyronitrile) under argon in a sealed tube at 130 °C for 3 h, followed by standard work-up, led to liquid olefin **4b**.

2-Octenes (4c and 5c), prepared from a 1.3:1 **4a–5a** mixture, methylmagnesium bromide, and (tpp)$_2$NiCl$_2$: liquid olefin mixture (70%, based on NMR analysis); ^{1}H NMR (CCl$_4$) δ 0.86 (t, 3, *J* = 7 Hz, Me), 1.1–1.7 (m, 9, methylenes, olefinic Me), 1.7–2.2 (m, 2, allyl Hs), 5.3–5.5 (m, 2, olefinic Hs). **4c** (58% of mixture): ^{13}C

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NMR δ 14.0 (C-8), 17.8 (C-1), 22.7 (C-7), 29.4 (C-5), 31.6 (C-6), 32.7 (C-4), 124.3 (C-2), 131.5 (C-3). **5c** (42% of mixture): ^{13}C NMR δ 12.6 (C-1), 14.0 (C-8), 22.7 (C-7), 26.9 (C-4), 29.4 (C-5), 31.6 (C-6), 123.3 (C-2), 130.7 (C-3).

6-Acetoxy-2-hexenes (7a and 7b), prepared from dihydropyran (**6a**), methylmagnesium bromide, and (tpp)$_2$NiCl$_2$: liquid alcohol mixture (73%);[32] IR OH 3360 (br m), C=C 1660 (w) cm^{-1}; ^{1}H NMR (CCl$_4$) δ 1.3–1.8 (m, 5, CH$_2$, Me), 1.9–2.3 (m, 2, allyl Hs), 3.52 (t, 2, *J* = 6 Hz, OCH$_2$ of minor isomer), 3.53 (t, 2, *J* = 6 Hz, OCH$_2$ of major isomer), 5.3–5.5 (m, 2, olefinic Hs). (*Z*)-4-Hexen-1-ol (**7**, R = Me, R′ = OH) (76% of mixture): ^{13}C NMR δ 12.3 (C-6), 22.9 (C-3), 32.1 (C-2), 61.7 (C-1), 123.8 (C-5), 129.4 (C-4). (*E*)-4-Hexen-1-ol (**8**, R = Me, R′ = OH) (24% of mixture): ^{13}C NMR δ 17.5 (C-6), 28.5 (C-3), 32.1 (C-2), 61.7 (C-1), 124.7 (C-5), 130.3 (C-4).

Quenching of the Grignard reaction with acetic anhydride yielded a liquid ester mixture (74%):[33] ^{1}H NMR (CDCl$_3$) δ 1.4–1.8 (m, 5, CH$_2$, Me), 2.05 (s, 3, COMe), 1.9–2.2 (m, 2, allyl Hs), 4.05 (t, 2, *J* = 6 Hz, OCH$_2$), 5.2–5.6 (m, 2, olefinic Hs). **7a** (75% of mixture): ^{13}C NMR δ 12.5 (C-1), 20.8 (Me), 23.0 (C-4), 28.2 (C-5), 63.7 (C-6), 124.7 (C-2), 128.9 (C-3), 170.9 (C=O). **8a** (25% of mixture): ^{13}C NMR δ 17.7 (C-1), 20.8 (Me), 28.2 (C-5), 28.7 (C-4), 63.7 (C-6), 125.6 (C-2), 129.7 (C-3), 170.9 (C=O).

The reaction between dihydropyran (**6a**) and methylmagnesium bromide in the presence of dpppNiCl$_2$, followed by acetylation, gave liquid ester **7a** (80%): ^{1}H NMR (CDCl$_3$) δ 1.60 (dd, 3, *J* = 7, 2 Hz, Me), 1.70 (quint, 2, *J* = 7 Hz, C-5 Hs), 2.05 (s, 3, COMe), 2.12 (qd, 2, *J* = 7, 2 Hz, C-4 Hs), 4.05 (t, 2, *J* = 7 Hz, OCH$_2$), 5.36 (dtq, 1, *J* = 11, 7, 2 Hz, H-3), 5.48 (dqt, 1, *J* = 11, 7, 2 Hz, H-2).

5-Phenyl-(*Z*)-4-penten-1-ol (7b), prepared from dihydropyran (**6a**), phenylmagnesium bromide and (tpp)$_2$NiCl$_2$: liquid (64%);[34] IR OH 3330 (br m), C=C 1610 (w), 1505 (m), 1460 (m) cm^{-1}; ^{1}H NMR (CCl$_4$) δ 1.4–1.8 (m, 2, CH$_2$), 2.2–2.5 (m, 2, allyl Hs), 3.50 (t, 2, *J* = 6 Hz, OCH$_2$), 5.57 (dt, 1, *J* = 12, 6 Hz, H-4), 6.37 (d, 1, *J* = 12 Hz, H-5), 7.0–7.4 (m, 5, aromatic Hs); ^{13}C NMR δ 24.7 (C-3), 32.5 (C-2), 61.8 (C-1), 126.2 (para C), 127.8 (ortho C), 128.4 (meta C), 129.0 (C-4), 131.8 (C-5), 137.2 (ipso C); MS, *m*/*e* (relative intensity) 162 (M$^+$, 22), 129 (97), 128 (36), 117 (57), 116 (23), 115 (78), 91 (base), 85 (61). Anal. (C$_{11}$H$_{14}$O) C, H.

The reaction between dihydropyran (**6a**) and phenylmagnesium bromide in the presence of dpppNiCl$_2$ gave a liquid alcohol mixxture (80%): **7b** (95% of the mixture) and **8b** (5% of the mixture):[32] ^{1}H NMR (CCl$_4$) δ 1.4–1.8 (m, 2, CH$_2$), 2.1–2.4 (m, 2, allyl Hs), 3.57 (t, 2, *J* = 6 Hz, OCH$_2$), 5.8–6.5 (m, 2, olefinic Hs), 6.8–7.6 (m, 5, aromatic Hs); ^{13}C NMR δ 29.0 (C-3), 31.8 (C-2), 61.5 (C-1), 125.5 (ortho C), 126.4 (para C), 128.8 (meta C), 129.6 (C-4 or C-5), 129.8 (C-5 or C-4), 137.2 (ipso C).

7-Acetoxy-(*E*)-3-heptene (7c) and 5-acetoxy-1-pentene (7d), prepared from dihydropyran (**6a**), ethylmagnesium bromide, and (tpp)$_2$NiCl$_2$, followed by acetylation and product purification by distillation (without chromatography): liquid ester **7c** (33%)[35] [^{1}H NMR (CCl$_4$) δ 0.93 (t, 3, *J* = 7 Hz, Me), 1.1–2.4 (m, 6, methylenes), 1.93 (s, 3, COMe), 3.97 (t, 2, *J* = 6 Hz, OCH$_2$), 5.1–5.6 (m, 2, olefinic Hs); ^{13}C NMR δ 14.0 (C-1), 20.2 (C-2), 20.6 (Me), 23.2 (C-5), 28.3 (C-6), 63.6 (C-7), 127.1 (C-3), 132.3 (C-4), 170.5 (C=O)] and liquid ester **7d** (22%),[36] identical with a commercial sample.

The reaction between dihydropyran (**6a**) and ethylmagnesium bromide in the presence of dpppNiCl$_2$, followed by acetylation, gave esters **7c** (52%) and **7d** (10%). A reaction of **6a**, isopropylmagnesium bromide, and (tpp)$_2$NiCl$_2$ and subsequent acetylation afforded ester **7d** (60%), and one of **6a**, cyclohexylmagnesium bromide, and 1:1 tpp–NiCl$_2$ furnished the same ester (**7d**) (40%).

7-Acetoxy-3-methyl-(*E*)-3-heptene (**9**), prepared from 2-ethyldihydropyran (**6b**), methylmagnesium bromide, and dpppNiCl$_2$, followed by acetylation: liquid ester **9** (30%);[37] ^{1}H NMR (CDCl$_3$) δ 0.95 (t, 3, *J* = 7 Hz, Me), 1.5–2.1 (m, 9, methylenes, olefinic Me), 2.00 (s, 3, COMe), 4.02 (t, 2, *J* = 6 Hz, OCH$_2$), 5.10 (t, 1, *J* = 7 Hz, olefinic H); ^{13}C NMR δ 12.7 (C-1), 15.8 (3-Me), 20.9 (acetyl Me), 24.0 (C-5), 28.6 (C-6), 32.2 (C-2), 34.0 (C-7), 121.4 (C-4), 137.9 (C-3), 171.1 (C=O).

***o*-Propenylphenols 11a and 11b**, prepared from benzofuran (**10**), methylmagnesium bromide, and (tpp)$_2$NiCl$_2$: liquid mixture of phenols (75%).[38] **11a** (80% of mixture): ^{1}H NMR (CDCl$_3$) δ 1.68 (dd, 3, *J* = 7, 2 Hz, Me), 5.90 (dq, 1, *J* = 11, 7 Hz olefinic H), 6.39 (br d, 1, *J* = 11 Hz, benzal H), 6.8–7.6 (m, 4, aromatic Hs); ^{13}C NMR δ 14.4 (Me). **11b** (20% of mixture): ^{1}H NMR δ (CDCl$_3$) 1.83 (dd, 3, *J* = 7, 2 Hz, Me), 6.17 (dq, 1, *J* = 16, 7 Hz, olefinic H), 6.74 (br d, 1, *J* = 16 Hz, benzal H), 6.8–7.6 (m, 4, aromatic Hs); ^{13}C NMR δ 18.7 (Me).

A reaction between benzofuran (**10**) and methylmagnesium bromide in the presence of dpppNiCl$_2$ gave phenols **11a** (27%) and **11b** (54%), while exposure of *o*-(*Z*)-propenylphenol (**11a**) to methylmagnesium bromide and dpppNiCl$_2$ furnished a mixture of phenols **11a** (20%) and **11b** (60%).

***o*-Hydroxy-(*E*)-stilbene** (**11c**), prepared from benzofuran (**10**), phenylmagnesium bromide, and (tpp)$_2$NiCl$_2$: crystalline phenol **11c** (61%);[39] mp 147–148 °C (from CCl$_4$) (lit.[39] mp 147 °C), spectrally identical with authentic sample.

5-Acetoxy-2-pentenes (13a and 14a), prepared from dihydrofuran (**12a**), methylmagnesium bromide, and (tpp)$_2$NiCl$_2$, followed by acetylation and product purification by distillation (without chromatography): liquid 5:1 mixture (75%)[40] of esters **13a** and **14a**; IR C=O 1735 (s), 1610 (w), cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 1.60 (d, 3, *J* = 6 Hz, Me), 2.05 (s, 3, COMe), 2.2–2.5 (m, 2, CH$_2$), 4.12 (t, 2, *J* = 7 Hz, OCH$_2$), 5.2–5.8 (m, 2, olefinic Hs). 5-Acetoxy-(*Z*)-2-pentene (**13a**): ^{13}C NMR δ 12.7 (C-1), 20.8 (Me), 26.3 (C-4), 63.7 (C-5), 125.0 (C-2), 126.6 (C-3), 170.9 (C=O). 5-Acetoxy-(*E*)-2-pentene (**14a**): ^{13}C NMR δ 17.9 (C-1), 20.9 (Me), 31.8 (C-4), 64.0 (C-5), 126.1 (C-2), 127.7 (C-3), 170.9 (C=O).

The reaction between dihydrofuran (**12a**) and methylmagnesium bromide in the presence of dpppNiCl$_2$ and followup as above afforded a 1:1 mixture (73%) of esters **13a** and **14a**, while one between 2-methyldihydrofuran (**12b**) and isopropylmagnesium bromide under the influence of (tpp)$_2$NiCl$_2$ and followup as above furnished a 1:20 mixture (61%) of the esters. Finally, a reaction of 2-methyldihydrofuran (**12b**), ethylmagnesium bromide, and (tpp)$_2$NiCl$_2$ gave a 1:7 mixture (60%) of the two esters.

4-Phenyl-3-buten-1-ols (13b and 14b), prepared from dihydrofuran (**12a**), phenylmagnesium bromide, and (tpp)$_2$NiCl$_2$: liquid 4-phenyl-(*Z*)-3-buten-1-ol (**13b**) (71%);[15] IR OH 3330 (br s), C=C 1610 (w), 1430 (w) cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 2.58 (dq, 2, *J* = 7, 2 Hz, CH$_2$), 3.70 (t, 2, *J* = 7 Hz, OCH$_2$), 5.68 (dt, 1, *J* = 12, 7 Hz, olefinic H), 6.54 (br d, 1, *J* = 12 Hz, benzal H), 7.2–7.4 (m, 5, aromatic Hs); ^{13}C NMR δ 31.8 (C-2), 62.2 (C-1), 126.6 (para C), 128.0 (ortho C), 128.1 (C-3), 128.5 (meta C), 131.2 (C-4), 137.0 (ipso C). This was also the product (65%) of the reaction of dihydrofuran (**12a**), phenylmagnesium bromide, and a 1:1 tpp–NiCl$_2$ mixture.

A reaction between dihydrofuran (**12a**) and phenylmagnesium bromide in the presence of dpppNiCl$_2$ produced a mixture of **13b** (28%) and 4-phenyl-(*E*)-3-buten-1-ol (**14b**) (56%)[41] [^{1}H NMR (CDCl$_3$) δ 2.45 (dq, 2, *J* = 7, 2 Hz, CH$_2$), 3.70 (t, 2, *J* = 7 Hz, OCH$_2$), 6.18 (dt, 1, *J* = 16, 7 Hz, olefinic H), 6.46 (br d, 1, *J* = 16 Hz, benzal H), 7.2–7.4 (m, 5, aromatic Hs)], while a reaction under the same catalyst's influence between alcohol **13b** and phenylmagnesium bromide led to a mixture of alcohols **13b** (48%) and **14b** (32%).

5-Acetoxy-2-methyl-2-pentene (**15a**), prepared from 2-methyldihydrofuran (**12b**), methylmagnesium bromide, and dpppNiCl$_2$, followed by acetylation and product purification by distillation (without chromatography): liquid **15a** (60%);[42] IR

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C=O 1735 (s), C=C 1650 (w) cm^{-1}; ^{1}H NMR ($\mathrm{CDCl_3}$) δ 1.62, 1.70 (s, 3 each, methyls), 2.02 (s, 3, COMe), 2.1–2.5 (m, 2, $\mathrm{CH_2}$), 4.05 (t, 2, J = 7 Hz, $\mathrm{OCH_2}$), 5.10 (br t, 1, J = 7 Hz, olefinic H).

4-Phenyl-(*Z*)-3-penten-1-ol (15b) and 4-phenyl-4-penten-1-ol (16), prepared from 2-methyldihydrofuran (**12b**), phenylmagnesium bromide, and $\mathrm{(tpp)_2NiCl_2}$: liquid alcohol **15b** (56%);[43] IR OH 3340 (m), C=C 1595 (w) cm^{-1}; ^{1}H NMR ($\mathrm{CDCl_3}$) δ 2.03 (d, 3, J = 2 Hz, Me), 2.0–2.3 (m, 2, $\mathrm{CH_2}$), 3.52 (t, 2, J = 7 Hz, $\mathrm{OCH_2}$), 5.46 (tq, 1, J = 7, 2 Hz, olefinic H), 7.0–7.4 (m, 5, aromatic Hs); ^{13}C NMR δ 25.7 (C-5), 32.5 (C-2), 62.6 (C-1), 122.9 (C-3), 126.5 (para C), 127.7 (ortho C), 128.0 (meta C), 139.3 (ipso C), 141.6 (C-4). Liquid alcohol **16** (14%): IR OH 3340 (m), C=C 1640 (w) cm^{-1}; ^{1}H NMR ($\mathrm{CDCl_3}$) δ 1.65 (quint, 2, J = 6 Hz, $\mathrm{CH_2}$), 2.58 (t, 2, J = 6 Hz, allyl Hs), 3.60 (t, 2, J = 6 Hz, $\mathrm{OCH_2}$), 5.15, 5.18 (d, 1 each, J = 18 Hz, olefinic Hs), 7.1–7.5 (m, 5, aromatic Hs); ^{13}C NMR δ 31.1 (C-2 or C-3), 31.5 (C-3 or C-2), 62.3 (C-1), 112.4 (C-5), 125.9 (ortho C), 127.3 (para C), 128.2 (meta C), 140.9 (ipso C), 147.8 (C-4); MS, *m/e* (relative intensity) 162 ($\mathrm{M^+}$, 15), 131 (16), 118 (base), 117 (56). Anal. ($\mathrm{C_{11}H_{14}O}$) C, H.

4-Phenyl-(*E*)-3-penten-1-ol (15c), prepared along with **15b** and **16** from 2-methyldihydrofuran (**12b**), phenylmagnesium bromide, and $\mathrm{dpppNiCl_2}$: liquid mixture of alcohols **15b** (42%), **16** (7%), and **15c** (21%).[44]

6-Acetoxy-3-methyl-3-hexenes (15d and 15e), prepared along with esters **13a** and **14a** from 2-methyldihydrofuran (**12b**), ethylmagnesium bromide, and $\mathrm{dpppNiCl_2}$: liquid 7:1 mixture of reduction products (15%) (**14a** and **13a**) and 3:1 mixture of ethylation products (60%)[45] (**15d** and **15e**); IR OH 3400 (w), C=O 1730 (s), C=C 1630 (w) cm^{-1}. *Z* isomer (**15d**): ^{1}H NMR ($\mathrm{CDCl_3}$) δ 0.95 (t, 3, J = 7 Hz, Me of Et), 1.70 (s, 3, Me), 2.05 (s, 3, COMe), 1.8–2.4 (m, 4, allyl Hs), 4.05 (t, 2, J = 7 Hz, $\mathrm{OCH_2}$), 5.10 (br t, 1, J = 7 Hz, olefinic H); ^{13}C NMR δ 12.6 (C-1), 20.9 (acetyl Me), 22.7 (Me), 24.7 (C-2), 27.1 (C-5), 64.2 (C-6), 118.6 (C-4), 140.1 (C-3), 170.9 (C=O). *E* isomer (**15e**): ^{1}H NMR ($\mathrm{CDCl_3}$) δ 0.95 (t, 3, J = 7 Hz, Me of Et), 1.60 (s, 3, Me), 2.05 (s, 3, COMe), 1.8–2.4 (m, 4, allyl Hs), 4.05 (t, 2, J = 7 Hz, $\mathrm{OCH_2}$), 5.10 (br t, 1, J = 7 Hz, olefinic H); ^{13}C NMR δ 12.5 (C-1), 15.9 (Me), 20.9 (acetyl Me), 27.3 (C-5), 32.2 (C-2), 64.0 (C-6), 117.4 (C-4), 140.0 (C-3), 170.9 (C=O).

General Procedure for the Reactions of Aryl Ethers with Grignard Reagents. All reactions of phenylmagnesium bromide and aryl ethers were carried out under the conditions described for the chemistry of the enol ethers except for the exclusive use of $\mathrm{(tpp)_2NiCl_2}$ as catalyst and the extension of the reaction time to 72 h. The crude product was purified by chromatography on alumina (activity I).

β-Methylnaphthalene (17e), prepared from β-methoxynaphthalene (**17a**), methylmagnesium bromide, and $\mathrm{dpppNiCl_2}$: crystalline solid (15%) (75% recovery of **17a**), mp 35–36 °C, spectrally identical with an authentic sample. When the reaction was executed in refluxing toluene, the product was isolated in 40% yield (50% recovery of **17a**).

β-Phenylnaphthalene (17f),[46] mp 100–102 °C, was prepared from ether **17a**, β-naphthyl *p*-toluenesulfonate (**17b**), and β-naphthol (**17c**) in 77, 60, and 16% yields, respectively.

2,3-Diphenylnaphthalene (17g),[47] mp 85–86 °C, was prepared from 2,3-dimethoxynaphthalene (**17d**) (in 3:1 Grignard reagent–ether molar ratio) in 45% yield.

α-Phenylnaphthalene (18b) was prepared from α-methoxynaphthalene (**18a**) in 70% yield. The liquid product was spectrally identical with an authentic, commerical sample.

***p*-Methylbiphenyl (19d) and *m*-methylbiphenyl (19e)** were prepared from *p*- (**19a**) and *m*-cresyl ether (**19b**), respectively, in 20 and 16% yields (based on ^{1}H NMR analysis), respectively (the recovery of **19a** and **19b** amounting to 40 and 58%, respectively). The products were identical with authentic, commerical specimens.

***p*-Methoxybiphenyl (20b) and *p*-terphenyl (21)** were the products (33 and 24% yields, respectively) of the reaction of hydroquinone dimethyl ether (**20a**) (in 3:1 Grignard reagent–ether molar ratio) (7% recovery yield). The products were identical with authentic commercial samples. *p*-Terphenyl (**21**) also was the product (30% yield) of the reaction of **20d** (25% recovery yield).

***m*-Methoxybiphenyl (20e)** was preapred from resorcinol dimethyl ether (**20b**) (in 3:1 Grignard reagent–ether molar ratio) in 23% yield (56% recovery yield of **20b**). The product was identical with authentic, commercial product.

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