chloride and by modified procedures using 20–130 times more solvent and the following systems: CS_2–$SnCl_4$; benzene–$SnCl_4$; CS_2–$AlCl_3$; ethyl ether–$SnCl_4$.

Attempted Ring Cleavage and Closures of the Norbornane Skeleton by Organometallic Routes

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In earlier studies, it has been found that carbon–carbon bond cleavage with ring rupture occurs in cyclobutylmethyl Grignard reagents and other polar organometallics in which the metal is on a carbon atom adjacent to a strained ring.[2] In some systems, the reverse, an intramolecular addition to the carbon–carbon double bond, is observed.[2b,3]

Another strained cyclic system of interest is the bicyclo[2.2.1]heptyl system. Freeman and coworkers have found that reactions of 5-chloro- and 5-chloromethylnorbornene with sodium lead to ring-cleavage products, but that the saturated analogs show no such rearrangement.[2f,4] Most likely, a great deal of the driving force in these cases derives from formation of allylic carbanions or organosodium compounds, and possibly from the increased strain of norbornene over norbornane.[5] A similar lack of ring cleavage was noted in the norbornyllithium compound formed by addition of *t*-butyllithium to norbornene.[6]

We find, as did Freeman, that the reaction of norbornyl chloride with sodium produces no cleavage attributable to transient organosodium compounds. Furthermore, no evidence for ring cleavage is found on heating the Grignard reagent in tetrahydrofuran to 130° for 100 hr or 170° for 40 hr. In both cases, attack on solvent leads to destruction of the organometallic. Similar lack of ring cleavage is found with norbornyllithium in hydrocarbon or ethers under a variety of conditions.

Failure to observe cleavage in the norbornyl system might, in principle, be due either to the slowness of the reaction relative to other reaction pathways open to the

organometallic, or to thermodynamic stability of the norbornyl skeleton relative to the various alternative ring-cleaved systems (eq 1). For this reason, halides
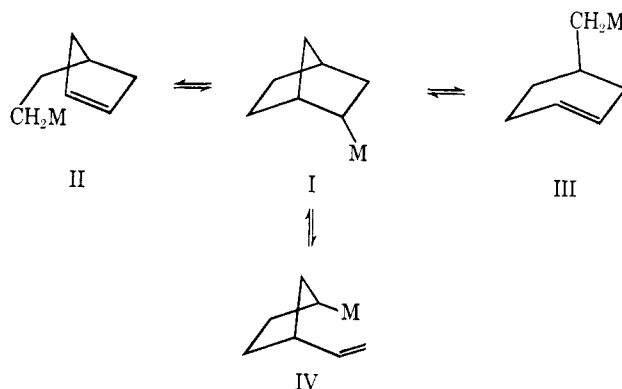
corresponding to organometallics II and III were prepared. It may be noted that the former carbonium ion cyclizes readily to norbornyl,[7] which suggests that such a cyclization of the organometallic *might* be energetically feasible.

The Grignard reagent from Δ³-cyclohexenylmethyl bromide was heated to 140–180°. The only products found were 4-methylcyclohexene and toluene. Similar results were obtained on heating the lithium reagent until it had pyrolized completely or on treating the bromide with sodium. Results are somewhat less conclusive with 2-(Δ³-cyclopentenyl)ethyl organometallics, owing to the strong tendency toward carbonium-ion cyclization. Hydrolysis of the Grignard reagent prepared from the bromide yielded 4-ethylcyclopentene and about 6% norbornene. After heating until most of the Grignard reagent had been destroyed by attack on solvent, about 9% norbornane was found. This may result from a small amount of cyclization under drastic conditions or simply from preferential norbornane formation by the norbornyl Grignard on reaction with the solvent. The original bromide contained about 5% norbornyl bromide. Formation of the lithium reagent, and reaction of the chloride with sodium likewise produced about 2–3% norbornane. At any rate, it may be concluded that, if cyclization of the cyclopentenylethyl system to norbornyl does occur by an organometallic route, the reaction is slow even under the most drastic conditions.

Recently, Richey[3] has reported that the Grignard reagent Vb from 6-bromo-1-heptene undergoes a facile ring closure to a mixture of *cis-* and *trans*-2-methylcyclopentylmethyl Grignard reagents (VIb) (eq 2). We
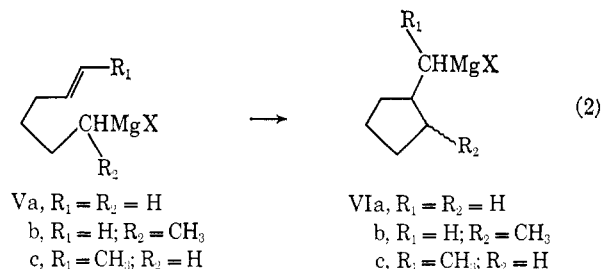
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(5) R. B. Turner, W. R. Meador, and R. E. Winkler, *J. Amer. Chem. Soc.*, **79**, 4116 (1957).

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Va, $R_1 = R_2 = H$
b, $R_1 = H$; $R_2 = CH_3$
c, $R_1 = CH_3$; $R_2 = H$

VIa, $R_1 = R_2 = H$
b, $R_1 = H$; $R_2 = CH_3$
c, $R_1 = CH_3$; $R_2 = H$

(7) (a) R. Lawton, *J. Amer. Chem. Soc.*, **83**, 2399 (1961); (b) P. D. Bartlett, S. Bank, R. J. Crawford, and G. H. Schmid, *ibid.*, **87**, 1288 (1965); (c) C. F. Wilcox and S. S. Chibber, *J. Org. Chem.*, **27**, 2332 (1962).

have found that the Grignard reagent Va from 6-chloro-1-hexene is also cyclized in refluxing tetrahydrofuran, although apparently at a much slower rate. In the former case, ring closure was nearly complete after 4-hr reflux, but, in the latter, we find an approximate half-life of about 125 hr under similar conditions. About 10% ring-closed product was observed immediately after formation of the Grignard reagent in ether or tetrahydrofuran,[8] suggesting that cyclization of a radical, free carbanion or "active unsolvated" organomagnesium[10] may occur during the formation of reagent.

Neither of the above instances is quite analogous to the hoped-for ring closure to norbornyl, since, in that case, the closure involves conversion of a primary Grignard reagent into a secondary one. Therefore, the reaction of the Grignard reagent Vc from 7-bromo-2-heptene was studied. Hydrolysis of the Grignard reagent in ether yielded a mixture of 97.5% 2-heptenes and 2.5% ethylcyclopentane either immediately after formation or after heating for 20 hr at 114°. At 155°, attack upon solvent became important, as evidenced by the presence of hydrocarbons in the ether solvent pumped off before hydrolysis of the Grignard reagent. Hydrolysis of the organometallic yielded the 2-heptenes and an amount of ethylcyclopentane dependent upon heating time. These hydrocarbons plus ethylidenecyclopentane were present in the volatiles removed before hydrolysis. Ring closure to the α-cyclopentylethyl Grignard reagent (VIc) thus occurs in competition with attack on solvent, and the ring-closed Grignard is subsequently consumed by solvent cleavage and by other reactions (possibly elimination of magnesium hydride) leading to ethylidenecyclopentane. An approximate analysis suggests that the ring closure has a half-life of about 40 hr at 155°. The ring closure is at least 90% in the direction to produce the α-cyclopentylethyl Grignard in preference to the less strained 2-methyl-cyclohexyl reagent. A preference for formation of the smaller ring has been noted previously.[2,3] However, the present instance is noteworthy, since the different rates of cyclization to primary and secondary organomagnesium compounds cannot be invoked to explain the results. The preference in the direction of addition may be related to a necessity of maintaining π overlap of the double bond, while beginning formation of the new carbon–carbon bond, and possibly to the steric requirements of a concerted cyclic transition state.[2]

Returning to the problem of the norbornyl organometallics, it seems now quite clear that, even if ring closure to the norbornyl system is thermodynamically favorable, the reaction should be extremely slow, even without the added strain of norbornane. Steric restrictions of the bicyclic skeleton upon transition state geometry[2e] might still further depress the rates of ring closure and cleavage. From thermochemical data, it is possible to estimate that the equilibria of organometallics II and III with norbornyl should be roughly thermoneutral. The addition reaction (eq 3) should be
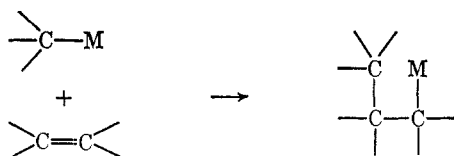
exothermic by approximately 20 kcal/mol, based on standard bond energy terms or upon Franklin's method[11] of estimating heats of combustion. The most reliable strain-energy estimate for norbornane appears to be a value of 18.5 kcal/mol from the heat of combustion.[12] Substances II, III, and IV should have strain energies of 3.8, 1.0, and 5.8 kcal,[13] and the difference in energy between secondary and primary organometallics may be taken as about 2.5 kcal/mol, as found by Applequist for the equilibration of alkyllithiums.[14] Combining the above estimates, the ring closure should be exothermic by 2.8, 0, and 7.3 kcal/mol for II, III, and IV, respectively, but entropy loss on cyclization would make the free energy of reaction less favorable. Thus, it appears that there is no large driving force for either cleavage or formation of the norbornane ring in an organometallic process.

Experimental Section

Spectra were obtained on Beckman IR-5 and Unicam SP 500 spectrometers and nmr spectra were obtained on a Varian A-60 spectrometer. Gas chromatographs were carried out using columns of Apiezon J, silicone grease, and Carbowax 20M on Chromosorb P. Preparation and handling of Grignard reagents was in the manner previously described.[2a]

Norbornyl Organometallics.—The Grignard reagent prepared from norbornyl chloride in tetrahydrofuran (1.4 M by nmr integration, 75% yield) was heated in a sealed nmr tube and the spectrum was examined periodically for changes. After 100 hr at 130°, the α-hydrogen absorption[15] had decreased to about one-third of its original size and, after a further 40 hr at 170°, had disappeared completely. A sharp new signal at δ (ppm) 5.36, attributed to ethylene,[15] gradually increased during the heating, but otherwise there were no new characteristic bands which might be assigned to isomeric Grignard reagents and no olefinic absorption other than that due to about 5% norbornene (δ 5.9) which had been present from the start. The sample tube was opened, and volatiles were removed without hydrolysis. Norbornane and norbornene were found in a ratio of 15:1. A small additional amount of norbornane was found on hydrolysis of the residue. No evidence was found for other hydrocarbons on three vpc columns. A similar result was obtained with the corresponding bromide.

A lithium reagent was prepared from norbornyl chloride in benzene at room temperature with high-speed stirring. Benzene solvent was removed under vacuum and replaced with pentane. The solvent fraction contained norbornane and norbornene in a ratio of about 1.5:1. Norbornane was the only hydrocarbon product detected in the pentane solution; however, no high-field nmr absorption attributable to the organolithium was observed. Based on gas chromatography after hydrolysis, the lithium reagent appeared to be formed in roughly 20% yield. Samples of the organolithium suspension were sealed in tubes and heated at 130°. The nmr spectrum of a sample heated for 44 hr showed new absorption at δ ~6.1 and 3, and removal of solvent under vacuum yielded a 2.9:1 ratio of norbornene to norbornane. Hydrolysis of the residue produced a negligible amount of product. Solvent was removed from a small sample of the alkyllithium suspension and replaced with ether. After a short period at room temperature, a small peak was observed in the nmr spectrum at about δ 5.4, attributable to ethylene. Norbornane was the only product detected on gas chromatography in the solvent

(8) Ring-closed products found by Lamb[9] on formation of the Grignard from the corresponding bromide are probably of similar origin.

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removed before hydrolysis, and a much smaller amount was found after hydrolysis of the residue. In a variety of other experiments involving formation of lithium reagent from norbornyl chloride and bromide, in ether and hydrocarbon solvents under a variety of conditions, no additional products were isolated; the same result was obtained on treatment of the Grignard reagent with an excess of butyllithium in dibutyl ether.

Norbornyl chloride was allowed to react with sodium, both at room temperature in 5% solution in pentane with fine sodium sand and high speed stirring and under Wurtz-type conditions (chunks of sodium with a small amount of hexadecane). The monomeric products in both cases contained only norbornane, norbornene, and nortricyclene in a very rough ratio of 65:25:10.

Δ^3-Cyclohexenylmethyl bromide and chloride were prepared from the corresponding alcohol: bromide, bp 70° (13 mm), $n^{23.5}$D 1.511 [lit.[16] bp 37° (2 mm), n^{25}D 1.5105]; chloride, bp 82° (40 mm), $n^{23.5}$D 1.4818 [lit.[17] bp 60–61° (13 mm), n^{23}D 1.4816].

Δ^3-Cyclohexenylmethyl Organometallics.—The Grignard reagent was prepared from the bromide (1.0 g) and sublimed magnesium (0.153 g) in tetrahydrofuran (4 ml). After removal of solvent under vacuum and replacement with fresh tetrahydrofuran, the nmr spectrum showed olefinic absorption at δ 5.57 and CH₂Mg at −0.42 (d, J = 6.2 Hz). No change was noted after 16 hr at 130°, but, after 23 hr at 180°, the α-hydrogen doublet had decreased in size and additional olefinic absorption appeared at δ 5.62 and ethylene at 5.38. After hydrolysis, 4-methylcyclohexane[18] and toluene were isolated by gas chromatography and identified by ir and nmr spectra. No other products were detected.

A lithium reagent was prepared from the chloride (2 g) and lithium (0.34 g) in a mixture of pentane (20 ml) and benzene (20 ml) with high-speed stirring. The solvent was removed under vacuum and replaced by pentane. An nmr spectrum of clear supernatant liquid showed olefinic absorption at δ 5.66 and a CH₂Li absorption at −0.71 (d, J = 6 Hz) calculated from a trace of benzene assumed to be at 7.27. On heating for 75 min at 150°, the CH₂Li absorption disappeared, the olefinic absorption broadened, and new weak absorption was visible at δ 7.13, 4.73, and 2.78. Solvent pumped from the heated lithium reagent contained 4-methylcyclohexene, toluene, and an unknown component of longer retention time in a ratio of 2.5:1.0:0.5. No volatile products were detected from hydrolysis of the residue. Additional experiments involving alkyllithium formation in ether or in hexadecane or treatment of a Grignard reagent with excess butyllithium in dibutyl ether failed to produce any evidence for formation of norbornane.

Treatment of the bromide with sodium similarly yielded only 4-methylcyclohexene and toluene in a ratio of 5.5:1.

2-(Δ^2-Cyclopentenyl)ethyl bromide and chloride were prepared from the corresponding alcohol.[7a] To a stirred solution of 2-(Δ^2-cyclopentenyl)ethanol[6a] (7.50 g, 0.067 mol) and 1.54 g (0.0195 mol) of pyridine in 20 ml of dry ether at −5°, phosphorus tribromide (7.57 g, 0.027 mol) in 5 ml of ether was added dropwise. The solution was refluxed 2 hr, filtered, washed with water and saturated sodium bicarbonate, and dried over sodium sulfate. Distillation yielded 3.70 g (32%): bp 68–70° (15 mm); n^{28}D 1.4967; ir (neat) 3060, 2930, 2840, 1615, 1447, 1353, 1260, 1230, 1217, 688 cm⁻¹; nmr (CCl₄) δ 1.8–2.8 (m, 7), 3.36 (t, 2, J = 7 Hz, CH₂Br), 5.63 (s, 2, olefinic). Contamination with a small amount of more volatile materials (determined by vpc) led to an unsatisfactory elemental analysis. About 5% norbornyl bromide was shown to be present by nmr absorption at δ 3.9 and by vpc.

2-(Δ^2-Cyclopentenyl)ethyl chloride was prepared with thionyl chloride in pyridine: bp 50° (12 mm). Only a single component appeared on gas chromatography, and, by nmr, the product was shown to contain about 3% norbornyl chloride.

Anal. Calcd for C₇H₁₁Cl: C, 64.37; H, 8.49. Found: C, 64.27; H, 8.46.

2-(Δ^2-Cyclopentenyl)ethyl Organometallics.—A Grignard reagent from 1.0 g of the bromide in tetrahydrofuran showed olefinic and CH₂Mg absorption at δ 5.59 and −0.59 (t, J = 8 Hz), respectively. After heating at 180°, the absorption de-

creased in intensity, and ethylene and new olefinic absorption appeared at δ 5.38 and 5.63. After hydrolysis, 4-ethylcyclopentene[19] and norbornane were found by gas chromatography to be present. The norbornane content increased from 6% before heating to 9% after heating until destruction of Grignard reagent was complete. This increase may represent a small amount of organometallic ring closure under drastic conditions or simply preferential loss of the primary Grignard by a route not producing the corresponding hydrocarbon.

The chloride was treated with metallic sodium under Wurtz-type conditions in a small amount of hexadecane. A minor gas chromatographic fraction (3%) corresponded in retention time to norbornane. Reaction of the chloride with tri-n-butyltin hydride neat yielded the same component (about 2%).

The chloride was treated with lithium in pentane with high-speed stirring. Either hydrolysis immediately or hydrolysis after heating 24 hr at 110° yielded a mixture of hydrocarbons which contained less than 5% norbornane.

5-Hexen-1-ol was prepared in 44% yield by reaction of the Grignard reagent from allyl chloride (54 g) with trimethylene oxide (38 g) in benzene–ether: bp 155–157° (lit.[20] bp 152–155°).

6-Chloro-1-hexene was prepared from the corresponding alcohol with thionyl chloride in pyridine in 62% yield: bp 125–127° (lit.[21] bp 128–130°).

Grignard Reagent from 6-Chloro-1-hexene.—A Grignard reagent prepared in tetrahydrofuran in the customary manner was maintained at reflux under nitrogen for 240 hr. Aliquots removed periodically were hydrolized and analyzed for 1-hexene and methylcyclopentane by gas chromatography. The original sample had about 90% 1-hexene and 10% methylcyclopentane, and the sample after 240 hr had the same hydrocarbons in a ratio of 23:77%. A Grignard reagent prepared in ether also contained about 10% ring-closed material, which was unchanged after 24 hr of reflux.

5-Hepten-1-ol.—2-Methyl-2-butene (0.66 mol) and sodium borohydride (0.25 mol) in dry diglyme (200 ml) were placed in a 1-l. flask at 0° under nitrogen. To this mixture was added 0.33 mol of boron trifluoride etherate over 1 hr. After an additional hour at 0°, a commercial sample of 1,5-heptadiene was added over 10 min. After 5 hr of additional stirring at 25°, a solution of 3 N sodium hydroxide (100 ml) and 30% hydrogen peroxide (100 ml) was added while the temperature was maintained below 50°. Stirring was continued an additional hour; the solution was diluted with saturated sodium chloride and extracted with ether. After two distillations, there was obtained 8.15 g (24%) of product: bp 75–77° (9 mm), n^{26}D 1.4375 [lit.[22] bp 77–78° (10 mm), n^{18}D 1.4446].

7-Bromo-2-heptene.—To a stirred solution of 5-hepten-1-ol (6.5 g, 0.057 mol) and pyridine (1.35 g, 0.0169 mol) in 75 ml of dry ether at 25°, phosphorus tribromide (5.73 g, 0.0211 mol) was added over 15 min. After stirring 9 hr at 25°, the mixture was filtered, the filtrate was washed with saturated sodium bicarbonate and water and dried, and the ether was evaporated. Traces of alcohol were removed by passing the product in pentane through alumina. Distillation yielded 3.6 g (36%): bp 70° (13 mm), n^{26}D 1.4674 [lit.[22] bp 63° (12 mm), n^{17}D 1.4702]. Only one peak appeared on gas chromatography (Carbowax 20M).

Grignard Reagent from 7-Bromo-2-heptene.—A Grignard reagent was prepared in the customary fashion in ether solution. The solvent was removed under vacuum and replaced with fresh ether, producing a solution about 0.15 M in reagent. Samples in sealed ampoules were heated and then analyzed by removal of solvent plus any volatile hydrocarbons, followed by hydrolysis of the residual organometallic. It was found by gas chromatographic separation and ir and nmr spectra that hydrolysis yielded 2-heptene (ir spectrum[23a] similar to a mixture reported as 90% *trans*) and ethylcyclopentane.[23b] Methylcyclohexane had a retention time similar to the latter, but examination of spectra indicated that the sample must contain less than 10%. The same components were present in the solvent removed before hydrolysis of the Grignard, in addition to a component of longer retention time identified as ethylidenecyclopentane by its ir spectrum.[23c] The hydrocarbons removed with the solvent increased

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with time at the expense of the 2-heptenes in the hydrolysate. The disappearance of hydrocarbon corresponding to unrearranged Grignard reagent had a half-life of about 12 hr at 155°, and, from the proportions of heptenes and cyclized materials in the solvent fraction, the half-life for cyclization was estimated as 39 hr, with a half-life of about 17.5 hr for attack on solvent. The Grignard reagent, as originally prepared, contained about 2.5% cyclized material, and no further change was noted after heating for 20 hr at 114°.

Registry No.—2-(Δ²-Cyclopentenyl)ethyl bromide, 21297-99-4; 2-(Δ²-cyclopentenyl)ethyl chloride, 21298-00-0.

Homogeneous Catalytic Hydrogenation of Unsaturated Organic Compounds[1]

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This paper describes an extensive investigation on the scope and limitations of tris(triphenylphosphine)chlororhodium(I) as a catalyst for homogeneous hydrogenation of unsaturated compounds in organic syntheses.[2] The literature to date deals with the feasibility of this catalyst for the hydrogenation of only simple olefins containing various reducible functional groups.[3-7] We have extended the scope of this catalyst for the reduction of highly substituted internal olefins containing a wide variety of reducible functional groups such as carboxylic acids, esters, aldehydes, ketones, nitriles, etc.

The hydrogenations were carried out in deoxygenated benzene or absolute ethanol at 40–60° and 60–100-psi pressure for 12–18 hr. The reaction products were studied by nmr and ir spectroscopy. In the case of incomplete hydrogenations the product ratio was calculated from the nmr spectra of the reaction mixtures. The results for α,β-unsaturated carboxylic acids and esters are summarized in Table I. The enormous synthetic utility of this catalyst for the reduction of a carbon–carbon double bond in the presence of carboxyl and ester functions is illustrated by the many successful reductions given in Table I.

The failure of 1-menthyl-α-phenylcinnamate to undergo hydrogenation can be attributed to steric hindrance. The results of hydrogenation of a number of α,β-unsaturated nitro compounds, aldehydes, ketones, and nitriles are given in Table II. The α,β-unsaturated nitro compounds underwent olefinic reduction rather smoothly. On the other hand, the reduction of α,β-unsaturated nitriles and ketones apparently depends on the steric influence of the olefinic substit-

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Reactant	Product	Yield, %	Reduction based on nmr and ir spectral analyses, %
Cinnamic acid	Hydrocinnamic acid	85	100
p-Methylcinnamic acid	p-Methylhydrocinnamic acid	90	100
α-Methylcinnamic acid	α-Methylhydrocinnamic acid	83	100
α-Phenylcinnamic acid	2,3-Diphenylpropionic acid	85	100
Itaconic acid	α-Methylsuccinic acid	92	100
Citraconic acid	α-Methylsuccinic acid	90	80
Ethyl cinnamate	Ethyl hydrocinnamate	93	100
1-Menthyl-α-phenylcinnamate	No reduction		

TABLE II

HYDROGENATION OF α,β-UNSATURATED NITRO COMPOUNDS, NITRILES, KETONES, AND ALDEHYDES

Reactant	Product	Yield, %	Reduction based on nmr and ir spectral analyses, %
p-Nitro-β-nitrostyrene	2-(p-Nitrophenyl)-nitroethane	60	100
3,4-Methylenedioxy-β-nitrostyrene	2-(3,4-Methylenedioxyphenyl)nitroethane	84	100
3-Methoxy-4-benzyloxy-β-nitrostyrene	2-(3-Methoxy-4-benzyloxyphenyl)-nitroethane	90	100
Cinnamonitrile	Hydrocinnamonitrile	86	100
2,3-Diphenylacrylonitrile	No reduction		
Benzal acetone	4-Phenyl-2-butanone	80	100
3,4-Diphenyl-3-buten-2-one	No reduction		
Cinnamaldehyde	60% hydrocinnamaldehyde and 40% ethylbenzene[a]	90	
o-Nitrocinnamaldehyde	60% o-nitrohydrocinnamaldehyde and 40% o-nitroethylbenzene[a]	70	
α-Methylcinnamaldehyde	No reduction		
p-Dimethylaminocinnamaldehyde	No reduction		

[a] Based on nmr spectral analyses.

uents. For instance, both cinnamonitrile and benzal acetone were readily reduced to hydrocinnamonitrile and 4-phenyl-2-butanone, respectively; however, the hydrogenation of more hindered disubstituted olefins such as 2,3-diphenylacrylonitrile and 3,4-diphenyl-3-