N-Allylhydroxylamines from 1,2-Addition of Allyl Grignard Reagents to Nitro Compounds: Generality and Drawbacks of the Reaction

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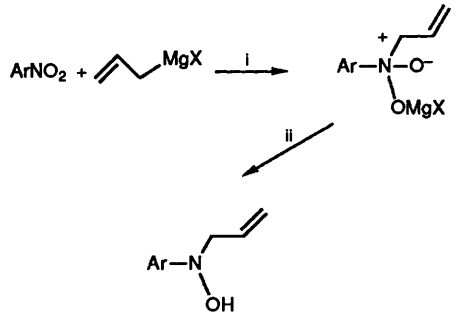
Allyl Grignard reagents react with both aromatic and aliphatic nitro derivatives *via* 1,2-addition to the nitro group. Conversely, nitroalkenes give either intractable mixtures or exclusive 1,4-conjugate addition. Nitroarenes with high steric hindrance at the *ortho* position and low aromatic stabilisation give competitive or exclusive conjugate addition at the reactive *para* position. The *'in situ'* treatment of the unstable 1,2-adducts with aluminium hydrides in the presence of catalytic amounts of palladium on charcoal provides a general method of synthesis of *N*-allylhydroxylamines. $LiAlH_4$ is a very efficient reducing agent, but, in some cases, it does not allow the reduction to be stopped at the hydroxylamino stage. Red-Al® and DIBAL-H are less efficient but they ensure greater selectivity. Red-Al avoids the complete reduction to amines except when a strongly electron-donating substituent such as a methoxy group is present in the *para* position of the aromatic ring. Hydroxylamines can be obtained by reaction of nitrosoarenes followed by aqueous quenching. However, this alternative reaction does not offer any improvement, since relevant amounts of azo and azoxy derivatives are recovered as by-products.

The course of the reaction of nitroarenes with Grignard reagents strongly depends on the nature of the carbanionic framework. Alkylmagnesium halides predominantly give conjugate addition, ultimately leading to ring-alkylated products.[1] Vinyl reagents[2] react *via* addition to the oxygen atoms of the nitro group, followed by decomposition of the unstable *O*-alkylated product to nitrosoarene. This compound reacts with vinyl reagents much faster than does the parent nitroarene, undergoing both normal and inverse addition and forming *N*-aryl-*N*-vinylhydroxylamino and *N*-aryl-*O*-vinylhydroxylamino magnesium salts respectively. The latter compounds afford indoles *via* a [3,3]sigmatropic rearrangement. The reactivity of aryl Grignard reagents is reported to be very similar to that of the vinyl analogues.[3] However, aryl derivatives add to nitrosoarene intermediates predominantly *via* normal addition.[3,4] A third reactivity pattern is represented by the formation of redox products such as nitroarene radical anions.[5] High temperatures,[5] polar solvents,[6] lithium derivatives,[5] hindered nitroarenes or reagents,[7] and highly electron-accepting nitroarenes[6] enhance this reaction.

In a recent preliminary communication,[8] we reported the occurrence of a fourth reactivity pathway: allylmagnesium halides attack the N=O double bond of the nitro group, very likely leading to an *N*-aryl-*N*-allyl-*N*-oxidohydroxylamino magnesium salt. This unstable intermediate can be quickly converted into the corresponding hydroxylamine by *in situ* treatment with lithium aluminium hydride in the presence of catalytic amounts of palladium on charcoal (Scheme 1).

These preliminary results were very surprising considering that, to our knowledge, every carbanionic moiety reacting with nitroarenic systems[1-9] gives either oxygen atom addition,[2,3,9c] or redox[1,5,7,10] or ring-alkylated products.[1,9] The reaction of allylmagnesium derivatives appeared to be of great potential in synthetic organic chemistry, since it represents the first approach to the preparation of *N*-allyl-*N*-arylhydroxylamines. However, in some cases the reduction of the hydroxylamino derivative to the corresponding aniline competed with reduction of the intermediate to hydroxylamine itself. Thus, a new selective reducing system able to give almost exclusive hydroxylamine formation would have synthetic utility. The aim of this paper is to study the generality of the reaction and on the precautions taken to avoid formation of anilines, which can be more easily prepared from standard methods.[11]

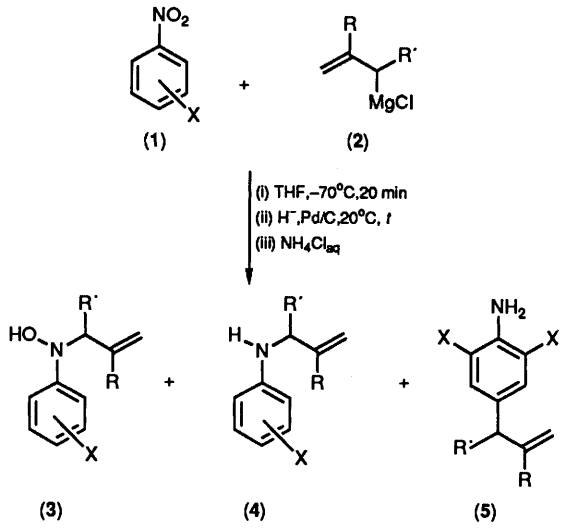


Scheme 1. *Reagents and conditions:* i, THF, −70 °C; ii, H^-, Pd/C, 20 °C.

Generality of the Reaction.—The reaction between allylmagnesium halides and nitroarenes was carried out at −70 °C and then lithium aluminium hydride and palladium on charcoal were added.[8] We observed that the reducing system is operative only at temperatures >0 °C. As a consequence, after addition of reagents the reaction mixture was allowed to warm to room temperature and was then stirred for 20 min before being quenched. Under these experimental conditions the reaction showed general characteristics such that good yields were obtained both with primary and secondary allyl reagents and with both aromatic and aliphatic nitro compounds (Table 1).

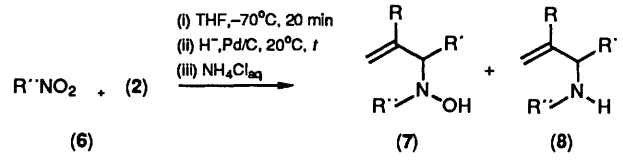
It should be noted that, although, in the equilibrium mixture of the Grignard reagents obtained starting from both 1-chlorobut-2-ene and 3-chlorobut-1-ene, the primary form prevails over the secondary[12] (Scheme 2), products arising exclusively from the latter form are recovered even in the presence of steric hindrance on the nitro group. Moreover, even

Table 1. Products and yields of the reaction between allyl Grignard reagents and nitro compounds in THF at −70 °C, followed by reduction with aluminium hydrides in the presence of catalytic amounts of Pd/C.



(A)

Entry	X	R	R′	H^-	t (min)	Yield (%) (3)	(4)	(5)
1	H	H	H	$LiAlH_4$	20	98[a]		
2	4-Cl	H	H	$LiAlH_4$	20	96[a]		
3	3-Cl	H	H	$LiAlH_4$	20	75[a]		
4	4-Ph	H	H	$LiAlH_4$	20	98[a]		
5	2-F	H	H	$LiAlH_4$	20	86[a]		
6	3-OMe	H	H	$LiAlH_4$	20	67[a]		
7	4-OMe	H	H	$LiAlH_4$	20		69[a]	
8	2-Me	H	H	$LiAlH_4$	20	64	8	
9	2-Me	H[b]	Me	$LiAlH_4$	20	60	9	
10	2-Me	Me	H	$LiAlH_4$	20	70	10	
11	2-Cl	Me	H	$LiAlH_4$	20	72		
12	2,6-Me_2	Me	H	$LiAlH_4$	20	51		18
13	2,6-Me_2	H[b]	Me	$LiAlH_4$	20	40		28
14	4-Cl-2-Pr^i	Me	H	$LiAlH_4$	120	80		
15	4-Cl-2-Pr^i	H[c]	Me	$LiAlH_4$	120	74		
16	2-OMe	H[c]	Me	$LiAlH_4$	20	30	28	
17	2-OMe	H[c]	Me	DIBAL-H[d]	90	33	38	
18	2-OMe	H[c]	Me	Red-Al®[e]	180	70	—	
19	4-OMe	H[c]	Me	Red-Al®	150		60	
20	2-Br	H[c]	Me	Red-Al®	150	25[f]		

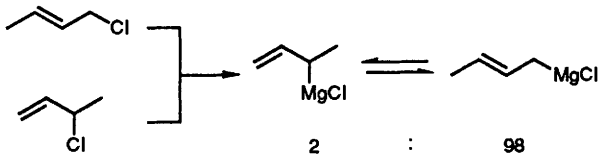


(B)

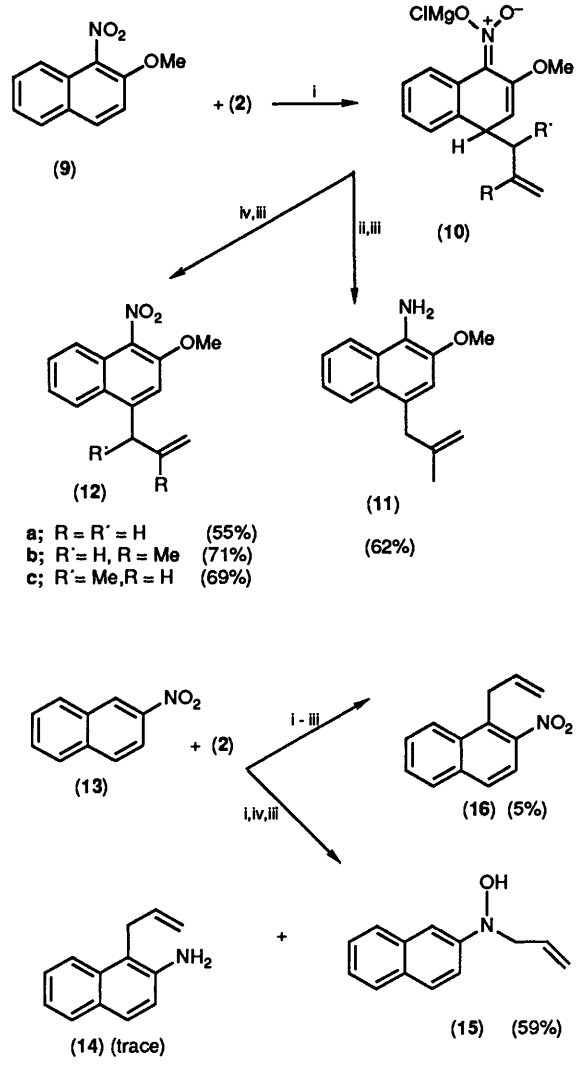
Entry	R″NO_2	R	R′	H^-	t (min)	Yield (%) (7)	(8)
21	2-Methyl-2-(2-nitroethyl)-1,3-dioxolane	Me	H	$LiAlH_4$	5	50	11
22	1-Nitrohexane	H[c]	Me	$LiAlH_4$	5	54	13
23	1-Nitrocyclohexane	H[b]	Me	$LiAlH_4$	5	63	10
24	1-Nitrohexane	H[c]	Me	DIBAL-H	120	63	
25	1-Nitrohexane	H[c]	Me	Red-Al®	180	65	
26	2-Nitroethyltetrahydropyranyl ether	H[c]	Me	Red-Al®	180	72	

[a] Data from ref. 8. [b] From 3-Chlorobut-1-ene. [c] From 1-Chlorobut-2-ene. [d] Di-isobutylaluminium hydride. [e] Bis-(2-methoxyethoxy)aluminium hydride. [f] Together with 70% of *N*-(but-3-en-2-yl)-*N*-phenylhydroxylamine.

when conjugate addition occurs (see later in the text), reaction products which can be considered to derive from the secondary derivative were always observed. For the sake of simplicity, in Table 1 the Grignard reagents which originated from both chlorides are depicted in this form.



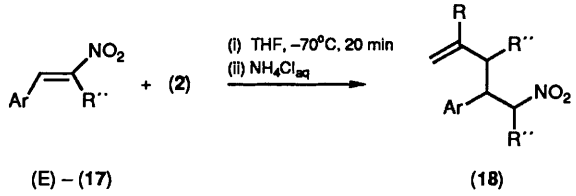
Scheme 2. *Reagents:* Mg, THF.



Scheme 3. *Reagents and conditions:* i, THF, −70 °C, 20 min; ii, $LiAlH_4$, Pd/C, 20 °C, 20 min; iii, aq. NH_4Cl; iv, DDQ, 0 °C, 3 h.

1,2-Addition completely or in part fails when the N=O double bond is sterically hindered by the presence of substituents on the *ortho* positions of the aromatic ring, and normal conjugate addition at the reactive *para* position of the ring is then favoured. In fact, while 2-nitrotoluene underwent 1,2-addition in 80% overall yield by β-methallylmagnesium chloride (Table 1, entry 10), 2-nitro-*m*-xylene with the same reagent gave 1,2-addition in 51% yield and ring alkylation in 18% yield (Table 1, entry 12). As expected, an increase in steric hindrance of the alkyl framework enhanced ring alkylation to the detriment of attack at the nitrogen atom. In the 2-nitro-*m*-xylene system

Table 2. Products and yields of the reaction between allyl Grignard reagents and nitroalkenes in THF at −70 °C, followed by aqueous quenching.



Entry	Ar	R″	R	R′	Yield (%)
1	*p*-Tolyl	H	H	H	75
2	*p*-Tolyl	H	H[a]	Me	78
3	Furyl	H	H[a]	Me	84
4	Butyl	H	H[a]	Me	*b*
5	$-CH_2CH_2CH_2CH_2-$		H	H	*b*

[a] From 1-chlorobut-2-ene. [b] No characterisable product was isolated.

conjugate addition accounted for 18 and 28% of the reaction when the entering group was a primary or a secondary framework, respectively (Table 1, entries 12 and 13). Furthermore, steric phenomena have more pronounced effects when the energy required for the destruction of the aromaticity is lower such as in a hindered naphthalene system: 2-methoxy-1-nitronaphthalene underwent almost exclusive conjugate addition (Scheme 3). On the other hand, in the less hindered 2-nitronaphthalene only traces of ring alkylation were observed *versus* 59% of *N*-alkylation.[8] The extent of ring alkylation was also verified by the more efficient oxidation of the nitronate intermediate with 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ).

We were surprised to observe that allyl Grignard reagents exclusively gave conjugate addition with nitroalkenes, although they are reported[13] to undergo both 1,2- and 1,4-addition by Grignard reagents. Excellent yields were obtained only in the presence of an aromatic nucleus in the β-position, while with aliphatic substituents in that position such as 1-nitrohex-1-ene and 1-nitrocyclohexene, polymerisation processes very likely occur leading to intractable reaction mixtures (Table 2). These results are in agreement with a recent report[14] on the reaction of nitroalkenes and aryl Grignard reagents.

Synthesis of N-*Allylhydroxylamines.*—As mentioned above, the present reaction is a very useful tool for the synthesis of *N*-allylhydroxylamines, since no alternative methods are available. As reported in Table 1, when electron-withdrawing groups are present in the aromatic ring hydroxylamines can be obtained free from the corresponding aniline. On the other hand, when an electron-donating substituent occupies a position conjugated with the nitro group, *N*-allylaniline formation cannot be avoided even when a slight excess of $LiAlH_4$ is used. For example, with 2-nitrotoluene *ca.* 10% yield of *N*-allyl-*o*-toluidine was recovered even when a stoicheiometric amount of hydride was employed (Table 1, entries 9 and 10). Aniline formation was strongly depressed by shortening the reaction time. However, the hydroxylamine yield decreased too and some quantity of the corresponding nitrone was observed. In previous work,[15] we found that in protic medium the 1,2-addition adduct of but-2-enylmagnesium chloride and 2-nitrotoluene eliminated a molecule of water to give a stable nitrone. As a consequence, the presence of a nitrone derivative among the reaction products confirms that the reduction process is

incomplete. With more strongly electron-donating substituents, aniline formation increases. In particular, in the reaction with 2-nitroanisole, a 28% yield of *N*-(but-3-enyl)-*o*-anisidine was recovered while in the reaction with 4-nitroanisole it was impossible to stop the reduction at the hydroxylamino stage (Table 1, entries 7 and 16). Amine formation was also observed in the aliphatic series (Table 1, entries 21–23).

In order to by-pass this drawback a screening of the available reducing agents was made. Only complex aluminium hydrides such as bis-(2-methoxyethoxy)aluminium hydride (Red-Al®) or di-isobutylaluminium hydride (DIBAL-H) in the presence of palladium on charcoal are able to accomplish the reduction, while other reducing systems such as $LiBH_4$, $NaBH_4$, Zn/AcOH, Zn/NH_4Cl fail. Both Red-Al and DIBAL-H require longer reaction times but they ensure greater selectivity. In fact, in the aliphatic series, the reduction stops at the hydroxylamino stage with both reagents (Table 1, entries 24–26). In the aromatic series Red-Al is much more selective than DIBAL-H; only the former compound is able to avoid complete reduction of 2-nitroanisole to *N*-allyl-*o*-anisidine, while with DIBAL-H a mixture of hydroxylamine and anisidine products is obtained (Table 1, entries 17 and 18). On the other hand, it was impossible to isolate the hydroxylamino derivative of 4-nitroanisole when using Red-Al too (Table 1, entry 19). Nevertheless, this reaction seems to be more complex since it required an abnormal excess of Grignard reagent (2.5 mol equiv. instead of 1.1 mol equiv.), but any attempt to understand the reasons for this anomaly was unsuccessful.

Finally, we tested the possibility of by-passing the reduction stage by starting from nitrosoarenes. Unfortunately, together with the hydroxylamine large amounts of azo and azoxy derivatives were isolated.[2b] As a consequence this reaction is less useful, since the synthesis of nitroso derivatives was tedious and better results were not obtained.

It should be noted that compounds arising from reduction of the double bond were never observed. Functions such as chloro, ethers, and dioxolanes are compatible with this reaction. Conversely, lithium aluminium hydride completely reduced the bromo function of 2-bromonitrobenzene, while with the more selective Red-Al 2-bromophenylhydroxylamine was isolated in 25% yield.

In conclusion the reaction of allyl Grignard reagents with nitro compounds, followed by reduction with aluminium hydrides in the presence of palladium on charcoal, provides a general method for the synthesis of the until now unavailable *N*-allylhydroxylamines. Only a few exceptions limit this procedure: *i.e.*, nitroalkenes and highly hindered nitroarenes give conjugate addition; while highly electron-donating substituents in a *para* position of an aromatic ring cause complete reduction to the aniline; finally a bromo function on the nitro derivative can be partly reduced.

Experimental

^1H NMR spectra were recorded with a Varian VXR 300 instrument. Chemical shifts are given in ppm from Me_4Si in $CDCl_3$ solutions. IR spectra were recorded with a Perkin-Elmer 257 spectrometer. VPC Analyses were performed on a Carlo Erba Fractovap 4160 HRGC instrument using an OV1 capillary column. Mass spectra were recorded with a VG 7070 spectrometer or with an HP 59970 workstation formed by an HP-5890 gas chromatograph equipped with a methylsilicone capillary column and by an HP-5970 mass detector. M.p.s are uncorrected and were determined with a Büchi apparatus. Tetrahydrofuran (THF) was dried by being refluxed over sodium wires until the blue colour of benzophenone ketyl persisted, and it was then distilling into a dry receiver under nitrogen. Commercial nitro derivatives and allyl chlorides were recrystallised or distilled before use.

Reaction of Allyl Grignard Reagents with Nitro Derivatives followed by Reduction.—General procedure. To a stirred THF solution (30 ml) of nitro compound (5 mmol) at −70 °C was added a solution of Grignard reagent (6 mmol) under nitrogen. The mixture was stirred for 20 min and then the appropriate hydride (7 mmol) and palladium on charcoal (0.7 mmol) were carefully added. The temperature was allowed to rise to 20 °C. After the appropriate reaction time (Table 1), the reaction mixture was quenched by careful addition of saturated aqueous ammonium chloride, filtered, and extracted with diethyl ether. The organic layer, dried over Na_2SO_4, was concentrated and submitted to a flash-chromatography purification on a silica gel column eluted with hexane–diethyl ether (4:1). Yields are reported in Table 1.

$NaBH_4$ or $LiBH_4$ in the presence of Pd/C or alone; $LiAlH_4$ alone; Zn/NH_4Cl or Zn/AcOH mixtures were unable to accomplish the reduction or led to an intractable reaction mixture.

The reaction of 2-nitrotoluene and the Grignard arising from but-2-enylchloride was quenched 5 min after the addition of the $LiAlH_4$–Pd/C mixture. The reaction mixture did not reveal the presence of *N*-(but-3-en-2-yl)-*o*-toluidine. After chromatographic separation of *N*-(but-3-en-2-yl)-*N*-(*o*-tolyl)-hydroxylamine (27%) and α-methyl-α-vinyl-*N*-(*o*-tolyl)nitrone (48%) were recovered. The nitrone was recognized by comparison with an authentic sample.[15] The following compounds were thus prepared.

N-*Allyl*-N-(o-*tolyl*)*hydroxylamine:* oil, δ_H 2.17 (s, 3 H, Me), 3.40–3.67 (m, 2 H, CH_2), 4.90–5.37 (m, 2 H, $=CH_2$), 5.60–6.30 (m, 1 H, –CH=), and 7.00–7.73 (m, 5 H, ArH + OH); *m/z* 163 (M^+), 147, 130, 118, 91, 77, and 65; ν_{max}(film) 3 230 br cm^{-1} (OH) (Found: C, 73.6; H, 8.0; N, 8.6. $C_{10}H_{13}NO$ requires C, 73.59; H, 8.03; N, 8.58%).

N-Allyl-*o*-toluidine: identified by comparison with an authentic sample prepared according to the literature.[16]

N-(*But*-3-*en*-2-*yl*)-N-(o-*tolyl*)*hydroxylamine:* m.p. 56 °C; δ_H 1.25 (d, *J* 6.85 Hz, 3 H, Me), 2.30 (s, 3 H, Me), 3.60–3.75 (m, 1 H, CH), 5.05–5.15 (m, 2 H, $=CH_2$), 5.50 (br s, 1 H, OH), 5.95–6.10 (m, 1 H, –CH=), and 7.00–7.50 (m, 4 H, ArH); *m/z* 177 (M^+), 160, 122, 91, 77, 65, and 55; ν_{max}(Nujol) 3 315br cm^{-1} (OH) (Found: C, 74.55; H, 8.55; N, 7.9. $C_{11}H_{15}NO$ requires C, 74.54; H, 8.53; N, 7.90%).

N-(*But*-3-*en*-2-*yl*)-o-*toluidine:* oil, δ_H 1.30 (d, *J* 6.85 Hz, 3 H, Me), 2.30 (s, 3 H, Me), 3.50 (br s, 1 H, NH), 3.65–3.75 (m, 1 H, CH), 5.00–5.15 (m, 2 H, $=CH_2$), 5.95–6.10 (m, 1 H, –CH=), and 7.05–7.52 (m, 4 H, ArH); *m/z* 161 (M^+), 146, 120, 106, 91, 77, and 65; ν_{max}(film) 3 425 cm^{-1} (NH) (Found: C, 81.95; H, 9.4; N, 8.65. $C_{11}H_{15}N$ requires C, 81.94; H, 9.38; N, 8.69).

N-*Methallyl*-N-(o-*tolyl*)*hydroxylamine:** oil, δ_H 1.90 (s, 3 H, Me), 2.30 (s, 3 H, Me), 3.45 (s, 2 H, CH_2), 4.90–5.10 (m, 2 H, $=CH_2$), 5.25 (br s, 1 H, OH), and 7.00–7.25 (m, 4 H, ArH); *m/z* 177 (M^+), 161, 160, 121, 91, 77, 65, and 55; ν_{max}(film) 3 300br cm^{-1} (OH) (Found: C, 74.5, H, 8.55; N, 7.9. $C_{11}H_{15}NO$ requires C, 74.54; H, 8.53; N, 7.90%).

N-*Methylallyl*-o-*toluidine:* oil, δ_H 1.90 (s, 3 H, Me), 2.35 (s, 3 H, Me), 3.45–3.55 (m, 3 H, CH_2 + NH), 5.00–5.15 (m, 2 H, $=CH_2$), and 7.00–7.35 (m, 4 H, ArH); *m/z* 161 (M^+), 146, 120, 106, 91, 77, and 65; ν_{max}(film) 3 427 cm^{-1} (NH) (Found: C, 81.9; H, 9.4; N, 8.7. $C_{11}H_{15}N$ requires C, 81.94; H, 9.38, N, 8.69%).

N-(2-*Chlorophenyl*)-N-*methallylhydroxylamine:* oil, δ_H 1.95 (s, 3 H, Me), 3.75 (s, 2 H, CH_2), 5.00–5.10 (m, 2 H, $=CH_2$), and 7.10–7.80 (m, 5 H, ArH + OH); *m/z* 197 (M^+), 199 (M^+

* Methallyl refers to 2-methylprop-2-enyl throughout.

+ 2), 180, 162, 141, 111, 77, 65, and 55; ν_{max}(film) 3 295br cm^{-1} (OH) (Found: C, 60.8; H, 6.1; N, 7.1. $C_{10}H_{12}ClNO$ requires C, 60.76; H, 6.12; N, 7.09%).

N-*Methallyl*-N-(2,6-*xylyl*)*hydroxylamine:* oil, δ_H 1.90 (s, 3 H, Me), 2.45 (s, 6 H, 2-, 6-Me), 3.85 (s, 2 H, CH_2), 4.95–5.10 (m, 2 H, $=CH_2$); 5.30 (br s, 1 H, OH), and 7.00–7.20 (m, 3 H, ArH); *m/z* 191 (M^+), 175, 174, 135, 118, 93, 91, and 77; ν_{max}(film) 3 395br cm^{-1} (OH) (Found: C, 75.3; H, 9.0, N, 7.3. $C_{12}H_{17}NO$ requires C, 75.35; H, 8.96; N, 7.32%).

2,6-*Dimethyl*-4-*methallylaniline:* oil, δ_H 1.65 (s, 3 H, Me), 2.20 (s, 6 H, 2-, 6-Me), 3.20 (s, 2 H, CH_2), 4.50–4.90 (m, 4 H, $=CH_2$ + NH_2), and 6.80 (s, 2 H, ArH); *m/z* 175 (M^+), 174, 161, 145, 115, 91, and 77; ν_{max}(film) 3 470 and 3 390 cm^{-1} (NH_2) (Found: C, 82.2; H, 9.8; N, 8.0. $C_{12}H_{17}N$ requires C, 82.23; H, 9.78; N, 7.99%).

N-(*But*-3-*en*-2-*yl*)-N-(2,6-*xylyl*)*hydroxylamine:* oil, δ_H 1.10 (d, *J* 6.80 Hz, 3 H, Me), 2.20 (s, 3 H, Me), 2.25 (s, 3 H, Me), 3.40–3.50 (m, 1 H, CH), 5.00–5.05 (m, 2 H, $=CH_2$), 5.45 (br s, 1 H, OH), 5.80–5.90 (m, 1 H, –CH=), and 6.95–7.10 (m, 3 H, ArH); *m/z* 191 (M^+), 176, 174, 158, 136, 118, 93, 91, and 77; ν_{max}(film) 3 290br cm^{-1} (OH) (Found: C, 75.3; H, 9.0; N, 7.3. $C_{12}H_{17}NO$ requires C, 75.35; H, 8.96; N, 7.32%).

4-(*But*-3-*en*-2-*yl*)-2,6-*dimethylaniline:* oil, δ_H 1.35 (d, *J* 6.85 Hz, 3 H, Me), 2.20 (s, 3 H, Me), 2.25 (s, 3 H, Me), 3.15–3.30 (m, 1 H, CH), 3.50 (br s, 2 H, NH_2), 5.00–5.10 (m, 2 H, $=CH_2$), 5.50–5.60 (m, 1 H, –CH=), and 6.60–7.00 (m, 2 H, ArH); *m/z* 175 (M^+), 174, 160, 130, 115, 91, 77, and 55; ν_{max}(film) 3 485 and 3 390 cm^{-1} (NH_2) (Found: C, 82.2; H, 9.8; N, 8.0. $C_{12}H_{17}N$ requires C, 82.23; H, 9.78; N, 7.99%).

N-(4-*Chloro*-2-*isopropylphenyl*)-N-*methallylhydroxylamine:* oil, δ_H 1.20 (d, *J* 7.15 Hz, 6 H, Me), 1.88 (s, 3 H, Me), 3.45 (septet, 1 H, CH), 3.85 (s, 2 H, CH_2), 5.00–5.10 (m, 2 H, $=CH_2$), 5.35 (br s, 1 H, OH), and 7.15–7.50 (m, 3 H, ArH); *m/z* 239 (M^+), 241 (M^+ + 2), 223, 198, 139, 110, 75, and 43; ν_{max}(film) 3 300br cm^{-1} (OH) (Found: C, 65.1; H, 7.55; N, 5.8. $C_{13}H_{18}ClNO$ requires C, 65.13; H, 7.57; N, 5.84%).

N-(*But*-3-*en*-2-*yl*)-N-(4-*chloro*-2-*isopropylphenyl*)*hydroxylamine:* oil, δ_H 1.15–1.23 (m, 9 H, Me), 3.38 (septet, *J* 6.75 Hz, 1 H, CH), 3.50–3.65 (m, 1 H, CH), 4.98–5.15 (m, 2 H, $=CH_2$), 5.45 (br s, 1 H, OH), 5.87–6.12 (m, 1 H, –CH=), and 7.10–7.30 (m, 3 H, ArH); *m/z* 239 (M^+); 241 (M^+ + 2), 223, 139, 110, 75, and 43; ν_{max}(film) 3 250br cm^{-1} (OH) (Found: C, 65.15; H, 7.6; N, 5.8. $C_{13}H_{18}ClNO$ requires C, 65.13; H, 7.57; N, 5.84%).

N-(*But*-3-*en*-2-*yl*)-N-(o-*methoxyphenyl*)*hydroxylamine:* oil, δ_H 1.25 (d, *J* 6.95 Hz, 3 H, Me), 3.97 (s, 3 H, OMe), 4.00–4.10 (m, 1 H, CH), 5.00–5.12 (m, 2 H, $=CH_2$), 5.50 (br s, 1 H, OH), 5.97–6.10 (m, 1 H, –CH=), and 6.85–8.15 (m, 4 H, ArH); *m/z* 193 (M^+), 177, 138, 120, 92, 77, 65, and 55; ν_{max}(film) 3 250br cm^{-1} (OH) (Found: C, 68.4; H, 7.85; N, 7.25. $C_{11}H_{15}NO_2$ requires C, 68.37; H, 7.82; N, 7.25%).

N-(*But*-3-*en*-2-*yl*)-o-*anisidine:* oil, δ_H 1.25 (d, *J* 6.90 Hz, 3 H, Me), 4.00 (s, 3 H, OMe), 4.10–4.25 (m, 2 H, CH + NH), 5.05–5.15 (m, 2 H, $=CH_2$), 5.90–6.15 (m, 1 H, –CH=), and 6.85–8.15 (m, 4 H, ArH); *m/z* 177 (M^+), 162, 136, 120, 93, 77, 65, and 55; ν_{max}(film) 3 420 cm^{-1} (NH) (Found: C, 74.5; H, 8.55; N, 7.9. $C_{11}H_{15}NO$ requires C, 74.54; H, 8.53; N, 7.9%).

N-(*But*-3-*en*-2-*yl*)-p-*anisidine:* oil, δ_H 1.20 (d, *J* 6.85 Hz, 3 H, Me), 3.60 (br s, 1 H, NH), 3.75 (s, 3 H, OMe), 3.90–4.00 (m, 1 H, CH), 5.00–5.10 (m, 2 H, $=CH_2$), 5.90–6.05 (m, 1 H, –CH=), and 6.80–7.10 (m, 4 H, ArH); *m/z* 177 (M^+), 162, 148, 130, 122, 108, 77, 65, and 55; ν_{max}(film) 3 425 cm^{-1} (NH) (Found: C, 74.55; H, 8.55; N, 7.9%).

N-(2-*Bromophenyl*)-N-(*but*-3-*en*-2-*yl*)*hydroxylamine:* oil, δ_H 1.25 (d, *J* 6.93 Hz, 3 H, Me), 3.90–4.00 (m, 1 H, CH), 4.95–5.05 (m, 2 H, $=CH_2$), 5.95–6.05 (m, 1 H, –CH=), 6.75 (br s, 1 H, OH), and 6.90–7.55 (m, 4 H, ArH); *m/z* 241 (M^+), 243 (M^+ + 2), 187, 170, 155, 130, 91, and 77; ν_{max}(film) 3 230br cm^{-1} (OH) (Found: C, 49.6; H, 5.05; N, 5.8. $C_{10}H_{12}BrNO$ requires C, 49.61; H, 5.00; N, 5.79%).

N-(*But*-3-*en*-2-*yl*)-N-*phenylhydroxylamine:* oil, δ_H 1.20 (d, *J* 6.90 Hz, 3 H, Me), 4.00–4.10 (m, 1 H, CH), 5.00–5.10 (m, 2 H, $=CH_2$), 5.90–6.05 (m, 1 H, –CH=), 6.75 (br s, 1 H, OH), and 6.95–7.45 (m, 5 H, Ph); *m/z* 163 (M^+), 148, 130, 109, 91, 77, and 55; ν_{max}(film) 3 230br cm^{-1} (OH); (Found: C, 73.6; H, 8.0; N, 8.6. $C_{10}H_{13}NO$ requires C, 73.59; H, 8.03; N, 8.58%).

4-(N-*Hydroxy*-N-*methallylamino*)*butan*-2-*one ethylene acetal:* oil, δ_H 1.40 (s, 3 H, Me), 1.85 (s, 3 H, Me), 2.10–3.80 (m, 6 H, CH_2), 3.95 (s, 4 H, OCH_2), 4.30 (br s, 1 H, OH), and 4.90–5.00 (m, 2 H, $=CH_2$); *m/z* 201 (M^+), 115, 110, 87, and 71; ν_{max}(film) 3 390br cm^{-1} (OH) (Found: C, 59.7; H, 9.5; N, 7.0. $C_{10}H_{19}NO_3$ requires C, 59.68; H, 9.52; N, 6.96%).

4-(N-*Methallylamino*)*butan*-2-*one ethylene acetal:* oil, δ_H 1.45 (s, 3 H, Me), 1.85 (s, 3 H, Me), 2.10–3.85 (m, 7 H, 3 × CH_2 + NH), 3.95 (s, 4 H, OCH_2), and 4.90–5.15 (m, 2 H, $=CH_2$); *m/z* 185 (M^+), 99, 87, 71, and 55; ν_{max}(film) 3 425 cm^{-1} (NH) (Found: C, 64.8; H, 10.35; N, 7.55. $C_{10}H_{19}NO_2$ requires C, 64.83; H, 10.34; N, 7.56%).

N-(*But*-3-*en*-2-*yl*)-N-*hexylhydroxylamine:* oil, δ_H 0.85 (t, *J* 7.00 Hz, 3 H, Me), 1.20 (d, *J* 6.55 Hz, 3 H), 1.25–2.70 (m, 10 H, CH_2), 3.35–3.45 (m, 1 H, CH), 5.05–5.15 (m, 2 H, $=CH_2$), 5.80–5.95 (m, 1 H, –CH=), and 6.80 (br s, 1 H, OH); *m/z* 171 (M^+), 154, 144, 100, 55, and 46; ν_{max}(film) 3 300br cm^{-1} (OH) (Found: C, 70.1; H, 12.35; N, 8.2. $C_{10}H_{21}NO$ requires C, 70.12; H, 12.36; N, 8.18%).

N-(*But*-3-*en*-2-*yl*)*hexylamine:* oil, δ_H 0.85 (t, *J* 7.00 Hz, 3 H, Me), 1.22 (d, *J* 6.55 Hz, 3 H), 1.25–2.10 (m, 8 H, CH_2), 2.50–2.80 (m, 3 H, NH + CH_2), 3.30–3.35 (m, 1 H, CH), 5.05–5.15 (m, 2 H, $=CH_2$), and 5.80–5.95 (m, 1 H, –CH=); *m/z* 155 (M^+), 154, 113, 86, 72, and 55; ν_{max}(film) 3 430 cm^{-1} (NH) (Found: C, 77.35; H, 13.65; N, 9.0. $C_{10}H_{21}N$ requires C, 77.35; H, 13.63, N, 9.02%).

N-(*But*-3-*en*-2-*yl*)-N-*cyclohexylhydroxylamine:* oil, δ_H 1.30 (d, *J* 6.85 Hz, 3 H), 1.50–2.85 (m, 11 H, aliph), 3.60–3.70 (m, 1 H, CH), 4.50 (br s, 1 H, OH), 5.15–5.20 (m, 2 H, $=CH_2$), and 5.85–6.00 (m, 1 H, –CH=); *m/z* 169 (M^+), 153, 152, 126, 113, 83, 72, and 55; ν_{max}(film) 3 300br cm^{-1} (OH) (Found: C, 71.0; H, 11.3; N, 8.25. $C_{10}H_{19}NO$ requires C, 70.96; H, 11.31; N, 8.27%).

N-(*But*-3-*en*-2-*yl*)*cyclohexylamine:* oil, δ_H 1.25 (d, *J* 6.90 Hz, 3 H), 1.50–2.00 (m, 10 H, aliph), 2.60–2.70 (m, 1 H, CH), 3.50–3.65 (m, 2 H, CH + NH), 5.10–5.20 (m, 2H, $=CH_2$), and 5.85–6.00 (m, 1 H, –CH=); *m/z* 153 (M^+), 152, 126, 113, 83, and 55; ν_{max}(film) 3 420 cm^{-1} (NH) (Found: C, 78.4; H, 12.5; N, 9.1. $C_{10}H_{19}N$ requires C, 78.37; H, 12.49; N, 9.14%).

N-(*But*-3-*en*-2-*yl*)-N-(2-*hydroxyethyl*)*hydroxylamine tetrahydropyranyl ether:* oil, δ_H 1.22 (d, *J* 6.85 Hz, 3 H), 1.45–1.90 (m, 6 H, aliph), 2.75–3.15 (m, 2 H), 3.30 (quintet, *J* 6.65 Hz, 1 H), 3.45–3.52 (m, 1 H), 3.65–3.73 (m, 1 H), 3.80–3.96 (m, 2 H), 4.60–4.65 (m, 1 H), 5.10–5.20 (m, 2 H, $=CH_2$), 5.60 (br s, 1 H, OH), and 5.80–5.95 (m, 1 H, –CH=); *m/z* 199 (M^+ − 16), 168, 144, 131, 100, 85, and 55; ν_{max}(film) 3 400br cm^{-1} (OH) (Found: C, 61.4; H, 9.8; N, 6.5. $C_{11}H_{21}NO_3$ requires C, 61.37; H, 9.83; N, 6.51%).

1-*Amino*-4-*methallyl*-2-*methoxynaphthalene:* oil, δ_H 1.80 (s, 3 H, Me), 3.75 (s, 2 H, CH_2), 3.95 (s, 3 H, OMe), 4.20 (br s, 2 H, NH_2), 4.70–4.95 (m, 2 H, $=CH_2$), and 7.40–8.00 (m, 5 H, ArH); *m/z* 227 (M^+), 212, 186, 184, 168, 152, 143, 115, 91, and 77; ν_{max}(film) 3 450 and 3 390 cm^{-1} (NH_2) (Found: C, 79.3; H, 7.55; N, 6.15. $C_{15}H_{17}NO$ requires C, 79.26; H, 7.54; N, 6.16%).

Reaction of Allyl Grignard Reagents with Hindered Nitro Derivatives followed by Oxidation.—To a stirred THF solution (30 ml) of nitro compound (5 mmol) at −70 °C was added a solution of Grignard reagent (6 mmol) under nitrogen. The mixture was stirred for 20 min and then a solution of DDQ (7

mmol) in THF (10 ml) was added. The temperature was allowed to rise to 20 °C. After 3 h, the reaction mixture was quenched by addition of saturated aqueous ammonium chloride, filtered, and extracted with diethyl ether. The organic layer, dried over Na_2SO_4, was concentrated and submitted to flash-chromatography purification on a silica gel column eluted with hexane–diethyl ether (9:1). The following compounds were thus prepared.

1-*Allyl*-3-*methoxy*-4-*nitronaphthalene* (55%), m.p. 51–53 °C; δ_H 3.65–3.75 (m, 2 H, CH_2), 4.00 (s, 3 H, OMe), 4.90–5.20 (m, 2 H, $=CH_2$), 5.70–6.30 (m, 1 H, –CH=), 7.10 (s, 1 H, 2-H), and 7.30–8.00 (m, 4 H, ArH); ν_{max}(KBr) 1 530 cm^{-1} (NO_2) (Found: C, 69.1; H, 5.4; N, 5.75. $C_{14}H_{13}NO_3$ requires C, 69.12; H, 5.39; N, 5.76%).

1-*Methallyl*-3-*methoxy*-4-*nitronaphthalene* (71%), oil, δ_H 1.80 (s, 3 H, Me), 3.80 (s, 2 H, CH_2), 4.05 (s, 3 H, OMe), 4.60–4.95 (m, 2 H, $=CH_2$), and 7.40–8.00 (m, 5 H, ArH); ν_{max}(film) 1 510 cm^{-1} (NO_2) (Found: C, 70.0; H, 5.9; N, 5.45. $C_{15}H_{15}NO_3$ requires C, 70.02; H, 5.88; N, 5.44%).

1-(*But*-3-*en*-2-*yl*)-3-*methoxy*-4-*nitronaphthalene* (69%), oil, δ_H 1.55 (d, *J* 6.85 Hz, 3 H, Me), 3.75–3.90 (m, 1 H, CH), 4.05 (s, 3 H, OMe), 5.15–5.25 (m, 2 H, $=CH_2$), 6.10–6.20 (m, 1 H, –CH=), and 7.45–8.15 (m, 5 H, ArH); ν_{max}(film) 1 525 cm^{-1} (NO_2) (Found: C, 70.05; H, 5.9, N, 5.4%).

1-*Allyl*-2-*nitronaphthalene* (5%), oil, δ_H 3.85–3.95 (m, 2 H, CH_2), 4.80–5.20 (m, 2 H, $=CH_2$), 5.70–6.30 (m, 1 H, –CH=), and 7.20–8.20 (m, 6 H, ArH); ν_{max}(film) 1 590 cm^{-1} (NO_2) (Found: C, 73.25; H, 5.2; N, 6.55. $C_{13}H_{11}NO_2$ requires C, 73.23; H, 5.20; N, 6.57%).

Reaction of Allyl Grignard Reagents with Nitroalkenes.—Nitroalkenes were prepared according to the literature procedure.[17] Only the (*E*)-isomer was isolated (coupling constant of the olefinic protons *ca.* 13 Hz).

To a stirred THF solution (30 ml) of nitro compound (5 mmol) at −70 °C was added a solution of Grignard reagent (6 mmol) under nitrogen. The mixture was stirred for 20 min and then the reaction mixture was quenched by addition of saturated aqueous ammonium chloride, filtered, and extracted with diethyl ether. The organic layer, dried over Na_2SO_4, was concentrated and submitted to flash-chromatography purification on a silica gel column eluted with hexane–diethyl ether (9:1). 1-Nitrohex-1-ene and 1-nitrocyclohexene gave rise to an intractable reaction mixture. Yields are reported in Table 2.

4-(4-*Methylphenyl*)-5-*nitropent*-1-*ene:* oil, δ_H 2.30 (s, 3 H, Me), 2.40–2.55 (m, 2 H, CH_2), 3.45–3.60 (m, 1 H, CH), 4.50–4.65 (m, 2 H, CH_2NO_2), 5.05–5.15 (m, 2 H, $=CH_2$), 5.60–5.75 (m, 1 H, –CH=), 7.05–7.15 (m, 4 H, ArH); *m/z* 188 (M^+ − 17), 164, 158, 143, 118 (base), 105, 91, and 77; ν_{max}(film) 1 545 cm^{-1} (NO_2) (Found: C, 70.2; H, 7.4; N, 6.85. $C_{12}H_{15}NO_2$ requires C, 70.22; H, 7.37; N, 6.82%).

3-*Methyl*-4-(4-*methylphenyl*)-5-*nitropent*-1-*ene:* oil, δ_H 1.25 (d, *J* 7.00 Hz, 3 H, Me), 2.35 (s, 3 H, Me), 2.40–2.55 (m, 1 H, CH_2), 3.45–3.65 (m, 1 H, CH), 4.52–4.65 (m, 2 H, CH_2NO_2), 5.05–5.15 (m, 2 H, $=CH_2$), 5.60–5.75 (m, 1 H, –CH=), and 7.05–7.15 (m, 4 H, ArH); *m/z* 164 (M^+ − 55), 158, 148, 143, 118 (base), 105, 91, and 77; ν_{max}(film) 1 545 cm^{-1} (NO_2) (Found: C, 71.2; H, 7.8; N, 6.4. $C_{13}H_{17}NO_2$ requires C, 71.21; H, 7.81; N, 6.39%).

4-(2-*Furyl*)-3-*methyl*-5-*nitropent*-1-*ene:* δ_H 1.05 (d, *J* 6.85 Hz, 3 H, Me), 2.30–2.65 (m, 2 H, CH–CH), 4.55–4.65 (m, 2 H, CH_2NO_2), 5.05–5.15 (m, 2 H, $=CH_2$), 5.60–5.75 (m, 1 H, –CH=), 6.10–6.15 (m, 1 H), 6.35–6.40 (m, 1 H), and 7.30–7.35 (m, 1 H); *m/z* 148 (M^+ − 47), 133, 105, 94 (base), 81, and 65; ν_{max}(film) 1 500 cm^{-1} (NO_2) (Found: C, 61.55; H, 6.7; N, 7.15. $C_{10}H_{13}NO_3$ requires C, 61.53; H, 6.71; N, 7.17%).

Reaction of Allyl Grignard Reagent with Nitrosobenzene and Nitrosotoluene.—To a stirred THF solution (10 ml) of Grignard reagent (6 mmol) at −70 °C was added a solution of nitroso compound (5 mmol) in THF (30 ml) under nitrogen. The mixture was stirred for 20 min and then was quenched by addition of saturated aqueous ammonium chloride, filtered, and extracted with diethyl ether. The organic layer, dried over Na_2SO_4, was concentrated and submitted to flash-chromatography purification on a silica gel column eluted with hexane–diethyl ether (9:1) to give the following product distributions: azobenzene (7%), azoxybenzene (32%), *N*-allyl-*N*-(phenyl)-hydroxylamine (29%), *o,o*-azotoluene (8%), *o,o*-azoxytoluene (22%), and *N*-allyl-*N*-(*o*-tolyl)hydroxylamine (47%) respectively. All compounds were recognized by comparison with authentic samples.

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