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An Efficient Method for the Deallylation of Allyl Aryl Ethers Using Electrochemically Generated Nickel

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The allyl group has been frequently used in organic synthesis as a protecting group for alcohols and amines due to its stability under basic and acidic conditions.[1] Therefore, many deallylation methods have been reported.[1−5] The removal of the allyl group is usually effected by a two-step process involving isomerization of the allyl ether to the corresponding 1-propenyl ether followed by hydrolysis or oxidative cleavage. The isomerization step requires strong bases[1] or transition metal catalysts.[2−4] Various one-pot deallylation procedures have been recently reported.[5]

We recently reported the easy preparation of a highly reactive nickel by an electrochemical method.[6] Electrolysis was carried out in a DMF solution containing 0.3 M Et_4NBF_4 using an undivided cell with a platinum cathode and a nickel anode at constant current under an argon atmosphere to give a highly reactive nickel−DMF suspension without massive deposition. The Ullmann-type reaction involving oxidative addition reactions for halobenzenes with the electrogenerated nickel produced the corresponding biphenyls.

On the basis of the above background information, we now report the deallylation of aryl allyl ethers with electrogenerated nickel.

Results and Conclusion

Highly reactive nickel was prepared by electrolysis in a DMF solution containing 0.3 M tetraethylammonium tetrafluoroborate (Et_4NBF_4) under an argon atmosphere. The electrolysis was carried out at a constant current of 10 mA/cm^2 at 0 °C for 965 coulombs (ca. 3.5 h) using a platinum cathode (1 × 2 cm) and nickel anode (1 × 2 cm) and produced 2 mmol of an active nickel−DMF suspension (Figure 1).

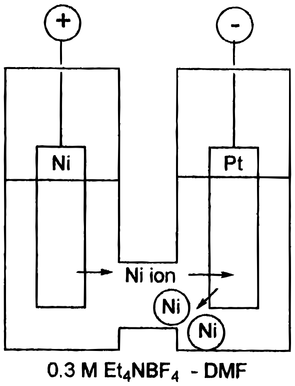
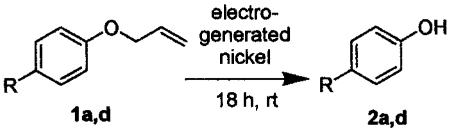


Figure 1. Apparatus of electrolysis for generation of active nickel.

Table 1. Deallylation of 1a,d with Electrogenerated Nickel and Additives in DMF



entry no	R	nickel (eq.)	additive	yield (%)
1	CO_2Me	2	-	44 (27) [a]
2	CO_2Me	4	-	50 (26) [a]
3	CO_2Me	4	K_2CO_3	71 (17) [a]
4	CO_2Me	4	NaH	55 (30) [a]
5	CO_2Me	4	Et_3N	66 (16) [a]
6	CO_2Me	4	AcONa	94
7	CO_2Me	2	AcONa	32 (55) [a]
8	CN	4	-	90
9	CN	4	AcONa	94

[a] Figures in parentheses are recovery yields of starting materials

The nickel−DMF suspension was transferred to a reaction flask using a syringe and then used for the deallylation of the allyl aryl ethers. At first, the deallylation conditions were investigated. As shown in Table 1, the deallylation of methyl 4-allyloxybenzoate (**1a**) using 2 and 4 equiv of the electrogenerated nickel proceeded with an approximate 50% yield. In the presence of K_2CO_3, NaH, Et_3N, and AcONa, the deallylation yields improved. Although the deallylation using 2 equiv of nickel in the presence of NaOAc gave **2a** in 35% yield, the reaction using 4 equiv of nickel and NaOAc at room temperature for 18 h produced the product in a 94% yield (Table 1, entry 6). However, the deallylation of 4-allyloxybenzonitrile (**1d**) gave **2d** in high yield without NaOAc (Table 1, entry 8). On the basis of these results, NaOAc is always added to the reaction mixture, although there were some cases in which NaOAc was not required.

As shown in Table 2, the deallylation of various allyl aryl ethers using electrogenerated nickel proceeded in good yields without affecting the methoxycarbonyl, cyano, acetyl, formyl, chloro, bromo, and alkenyl groups. Also the deallylation was not affected by other O-protecting groups such as the benzyl, tosyl, and tetrahydropyranyl groups. However, the deallylation of 4-allyloxyiodobenzene gave the corresponding phenol in low yields, because

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[1] Green, T. W.; Wuts, P. G. M. *Protective Groups in Organic Synthesis*, 2nd ed.; Wiley: New York, 1991.

[2] Pd/C: Boss, R.; Scheffold, R. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2056; Carles, H. A.; Haywood, D. J. *J. Chem. Soc., Chem. Commun.* **1980**, 980.

[3] $(PPh_3)_3RhCl$: Boons, G.-J. *J. Chem. Soc., Chem. Commun.* **1996**, 141.

[4] $[Ir(COD)(PMePh_2)_2]PF_6$: Baudry, D.; Ephritikhine, M.; Felkin, H. *J. Chem. Soc., Chem. Commun.* **1978**, 694. Oltvoort, J. J.; van Boechel, C. A. A.; de Koning, J. H.; van Boom, J. H. *Synthesis* **1981**, 305.

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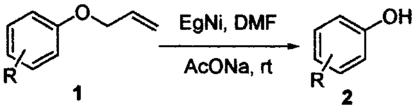
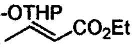
Table 2. Deallylation of Aryl Allyl Ethers with Electrogenerated Nickel

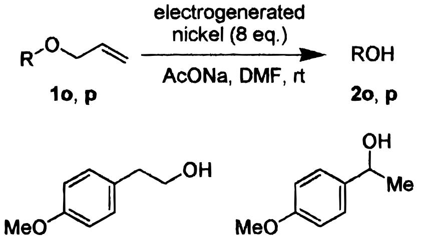


1 → 2

entry no	1	R	yield (%)
1	a	4-CO$_2$Me	94
2	b	3-CO$_2$Me	79
3	c	2-CO$_2$Me	77
4	d	4-CN	98
5	e	4-COMe	86
6	f	4-CHO	91
7	g	4-Cl	75
8	h	4-Br	72
9	i	4-I	11
10	j	4-OMe	76[b]
11	k	4-OBn	73 (21)[a]
12	l	4-OTs	99
13	m	4-OTHP	25 (51)[a]
14	n	4 	100

a Figures in parentheses are recovery yields of starting materials. b Using 10 equivalents active nickel.

Scheme 1. Deallylation of Primary and Secondary Allyloxy Substrates



2o (69 %) **2p** (70%)

the electrogenerated nickel has a high reactivity for the oxidative addition of the iodo group (Table 2, entry 2). As for the deallylation of aliphatic allyoxy substrates, the deprotection of primary (**1o**) and secondary (**1p**) allyloxy substrates with 8 equiv of electrogenerated nickel also gave the corresponding alcohols in 69 and 70% yields, although the deallylation with 4 equiv of nickel produced low yields (37% and 57%, respectively) (Scheme 1).

In summary, the deallylation of the allyl aryl ethers using a highly reactive nickel–DMF suspension, which was easily prepared by electrolysis, proceeds in the presence of NaOAc under mild conditions without affecting the various functional groups.

Experimental Section

All melting points and boiling points are uncorrected. The IR spectra were measured on a JASCO IR-810 spectrophotometer. ^{1}H NMR spectra were recorded on a Varian Gemini 2000 (300 MHz). Chemical shifts are expressed in δ (ppm) values with tetramethylsilane (TMS) as the internal reference, and coupling constants are expressed in hertz (Hz). The mass spectra (MS) and high-resolution mass spectra (HRMS) were recorded on JMS-DX303 and JMS-AX500 instruments, respectively.

Preparation of Electrogenerated Nickel. A platinum sheet (1×2 cm^2) as the cathode and a nickel sheet (1×2 cm^2) as the anode were placed in a 15 mL H-shaped undivided cell that contained 0.3 M Et$_4$NBF$_4$–DMF (8 mL). Electrolysis was carried out under an argon atmosphere at a constant current of 10 mA/cm^2 at 0 °C until 965 coulombs of electricity had passed to produce a black suspension containing the active nickel.

General Procedure for Deallylation of Allyl Aryl Ethers. The nickel–DMF suspension was added to an allyl aryl ether (0.5 mmol) and NaOAc (2.5 mmol) using a syringe under an argon atmosphere. The mixture was stirred for 18 h at room temperature. Then 2 M HCl (10 mL) was added to the reaction mixture. After the addition of Et$_2$O (20 mL) to the solution, the mixture was filtered through a Celite pad. The aqueous layer was extracted with Et$_2$O (10 mL $\times$ 3), and the ethereal layers were combined. The ethereal layer was washed with H$_2$O (20 mL $\times$ 3), dried over MgSO$_4$, and evaporated under reduced pressure. The residue was purified by recrystallization or distillation.

Methyl 4-hydroxybenzoate (2a): colorless needles from Et$_2$O–hexane; mp 124–125 °C (lit.[7] mp 127 °C); ^{1}H NMR (CDCl$_3$/TMS) δ 3.90 (s, 3 H), 6.77 (br, 1 H), 6.90 (d, $J = 8.8$ Hz, 2 H), 7.95 (d, $J = 8.8$ Hz, 2 H); IR ν (KBr) cm^{-1} 3300, 1690; MS m/z 152 (M$^+$).

Methyl 3-hydroxybenzoate (2b): colorless plates from Et$_2$O–hexane; mp 69–71 °C (lit.[7] mp 73 °C); ^{1}H NMR (CDCl$_3$/TMS) δ 3.92 (s, 3 H), 6.81 (br, 1 H), 7.07–7.11 (m, 1 H), 7.30 (t, $J = 7.7$ Hz, 1 H), 7.58–7.61 (m, 2H); IR ν (KBr) cm^{-1} 3370, 1700; MS m/z 152 (M$^+$).

Methyl 2-Hydroxybenzoate (2c): colorless liquid; bp 40–50 °C/3 mmHg (lit.[7] mp 222 °C/760 mmHg); ^{1}H NMR (CDCl$_3$/TMS) δ 3.95 (s, 3 H), 6.88 (dt, $J = 8.0$, 1.1 Hz, 1 H), 6.98 (dd, $J = 1.1$, 8.5 Hz, 1 H), 7.46 (ddd, $J = 8.5$, 8.0, 1.6 Hz, 1 H), 7.84 (dd, $J = 8.0$, 1.6 Hz, 1 H), 10.76 (s, 1 H); IR ν (KBr) cm^{-1} 3200, 1680; MS m/z 152 (M$^+$).

4-Hydroxybenzonitrile (2d): colorless plates from Et$_2$O–hexane; mp 109–110 °C (lit.[7] mp 112 °C); ^{1}H NMR (CDCl$_3$/TMS) δ 6.91 (d, $J = 8.2$ Hz, 2 H), 7.55 (d, $J = 8.2$ Hz, 2 H); IR ν (KBr) cm^{-1} 3290, 2230; MS m/z 119 (M$^+$).

4-Hydroxyacetophenone (2e): colorless prisms from Et$_2$O–hexane; mp 106–107 °C (lit.[7] mp 110 °C); ^{1}H NMR (CDCl$_3$/TMS) δ 2.57 (s, 3 H), 6.91 (d, $J = 8.8$ Hz, 2 H), 7.91 (d, $J = 8.8$ Hz, 2H); IR ν (KBr) cm^{-1} 3310, 1660; MS m/z 136 (M$^+$).

4-Hydroxybenzaldehyde (2f): colorless prisms from Et$_2$O–hexane; mp 110–112 °C (lit.[7] mp 118 °C); ^{1}H NMR (CDCl$_3$/TMS) δ 7.00 (d, $J = 8.5$ Hz, 2 H), 7.83 (d, $J = 8.5$ Hz, 2 H), 9.85 (s, 1 H); IR ν (KBr) cm^{-1} 3170, 1670; MS m/z 122 (M$^+$). Anal. Calcd for C$_7$H$_6$O$_2$: C, 68.85; H, 4.95. Found: C, 68.76; H, 5.05.

4-Chlorophenol (2g): colorless viscous liquid; bp 50–60 °C/3 mmHg (lit.[7] bp 220 °C/760 mmHg); ^{1}H NMR (CDCl$_3$/TMS) δ 5.81 (br, 1 H), 6.77 (d, $J = 8.8$ Hz, 2 H), 7.18 (d, $J = 8.8$ Hz, 2 H); IR ν (KBr) cm^{-1} 3340; MS m/z 128 (M$^+$).

4-Bromophenol (2h): colorless prisms; mp 63–64 °C (lit.[7] mp 66 °C); ^{1}H NMR (CDCl$_3$/TMS) δ 5.07 (br, 1 H), 6.73 (d, $J = 8.8$ Hz, 2 H), 7.34 (d, $J = 8.8$ Hz, 2 H); IR ν (KBr) cm^{-1} 3350; MS m/z 172 (M$^+$).

4-Iodophenol (2i): colorless prisms from Et$_2$O–hexane; mp 91–93 °C (lit.[7] mp 94 °C); ^{1}H NMR (CDCl$_3$/TMS) δ 5.09 (br, 1 H), 6.63 (d, $J = 8.8$ Hz, 2 H), 7.51 (d, $J = 8.8$ Hz, 2 H); IR ν (KBr) cm^{-1} 3360; MS m/z 220 (M$^+$).

4-Methoxyphenol (2j): colorless plates from Et$_2$O–hexane; mp 49–51 °C (lit.[7] mp 55–57 °C); ^{1}H NMR (CDCl$_3$/TMS) δ 3.76 (s, 3H), 4.79 (br, 1H), 6.78–6.82 (m, 4H); IR ν (KBr) cm^{-1} 3380; MS m/z 124 (M$^+$). Anal. Calcd for C$_7$H$_9$O$_2$: C, 67.73; H, 6.50. Found: C, 67.62; H, 6.48.

4-(Benzyloxy)phenol (2k): colorless plates from Et$_2$O–hexane; mp 119–120 °C (lit.[8] mp 122 °C); ^{1}H NMR (CDCl$_3$/TMS) δ 4.44 (s, 1 H), 5.01 (s, 2 H), 6.76 (d, $J = 9.1$ Hz, 2H), 6.86 (d, $J = 9.1$ Hz, 2 H), 7.34–7.41 (m, 5 H); IR ν (KBr) cm^{-1} 3400; MS m/z 200 (M$^+$).

4-Hydroxyphenyl 4-methyl-1-benzenesulfonate (2l): colorless solid; bp 205–215 °C/3 mmHg; ^{1}H NMR (CDCl$_3$/TMS) δ 2.45 (s, 3 H), 6.70 (d, $J = 8.8$ Hz, 2 H), 6.83 (d, $J = 8.8$ Hz, 2 H), 7.31 (d, $J = 8.5$ Hz, 2 H), 7.69 (d, $J = 8.5$ Hz, 2 H); IR ν (KBr)

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cm^{-1} 3400, 1370, 1170; MS *m*/*z* 264 (M$^+$). Anal. Calcd for $C_{13}H_{12}O_4S$: C, 59.08; H, 4.58; S, 12.13. Found: C, 59.00; H, 4.58; S, 11.88.

4-(Tetrahydro-2*H*-2-pyranyloxy)phenol (2m): colorless scales from Et_2O−hexane; mp 73−75 °C; ^{1}H NMR ($CDCl_3$/TMS) δ 1.65−1.73 (m, 3 H), 1.82−1.86 (m, 2 H), 1.91−2.05 (m, 1 H), 3.56−3.63 (m, 1 H), 3.91−3.99 (m, 1 H), 4.91 (br, 1 H), 5.28 (t, *J* = 8.8 Hz, 1 H), 6.74 (d, *J* = 8.8 Hz, 2 H), 6.93 (d, *J* = 8.8 Hz, 2 H); IR ν (KBr) cm^{-1} 3370; MS *m*/*z* 194 (M$^+$). Anal. Calcd for $C_{11}H_{14}O_3$: C, 68.02; H, 7.26. Found: C, 68.17; H, 7.33.

Methyl (*E*)-3-(4-hydroxyphenyl)-2-propenoate (2n): colorless prisms from Et_2O−hexane; mp 68−72 °C (lit.[9] bp 73 °C); ^{1}H NMR ($CDCl_3$/TMS) δ 1.33 (t, *J* = 7.1 Hz, 3 H), 4.26 (q, *J* = 7.1 Hz, 2 H), 4.61−5.81 (br, 1 H), 6.30 (d, *J* = 15.9 Hz, 1 H), 6.85 (d, *J* = 8.5 Hz, 2 H), 7.43 (d, *J* = 8.5 Hz, 2 H), 7.63 (d, *J* = 15.9, 1 H); IR ν (KBr) cm^{-1} 3270, 1680, 1630; MS *m*/*z* 192 (M$^+$).

2-(4-Methoxyphenyl)ethanol (2o): colorless liquid; bp 85−95 °C/3 mmHg; ^{1}H NMR ($CDCl_3$/TMS) δ 1.51 (br, 1 H), 2.81 (t, *J* = 6.6 Hz, 3 H), 3.79 (s, 3H), 3.82 (t, *J* = 6.6 Hz), 6.86 (d, *J* = 8.8 Hz, 2 H), 7.15 (d, *J* = 8.8 Hz, 2 H); IR ν (KBr) cm^{-1} 3350; MS *m*/*z* 52 (M$^+$). Anal. Calcd for $C_9H_{12}O_2$: C, 71.03; H, 7.95. Found: C, 71.29; H, 8.07.

1-(4-Methoxyphenyl)ethanol (2p): colorless liquid; bp 65−75 °C/3 mmHg; ^{1}H NMR ($CDCl_3$/TMS) δ 1.48 (d, *J* = 6.6 Hz, 3 H), 1.80 (br, 1 H), 3.81 (s, 3 H), 4.86 (q, *J* = 6.6 Hz, 1H), 6.89 (d, *J* = 8.8 Hz, 2 H), 7.30 (d, *J* = 8.8 Hz, 2 H); IR ν (KBr) cm^{-1} 3380; MS *m*/*z* 152 (M$^+$). Anal. Calcd for $C_{11}H_{14}O_3$: C, 68.02; H, 7.26. Found: C, 68.17; H, 7.33.

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