methanol was evaporated under reduced pressure. The crude residue was chromatographed on a silica gel (eluent; Hexane/EtOAc 10 : 1) to give 0.29 g (90%) of the pure N-methylaniline.[10]

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10. Spectral data: ^{1}H NMR (200 MHz, $CDCl_3$): δ 2.85 (S, 3 H), 6.61-6.76 (m, 3 H), 7.17-7.26 (m, 2 H); IR (neat) 3433 cm^{-1}; GCMS m/z (relative intensity) (EI, 70 eV) 107 (M^+ 82), 106 (100), 77 (29); Anal. Calcd for C_7H_9N: N, 13.07; C, 78.46; H, 8.47. Found: N, 13.12; C, 78.43; H, 8.46.

A Facile Synthesis of 7-Nitro-2,3-dihydrobenzo[*b*]furans

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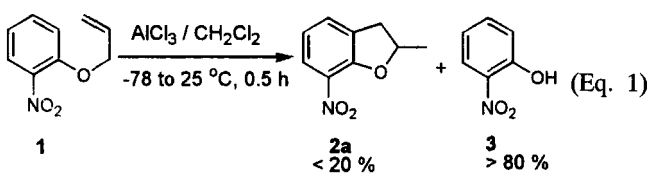
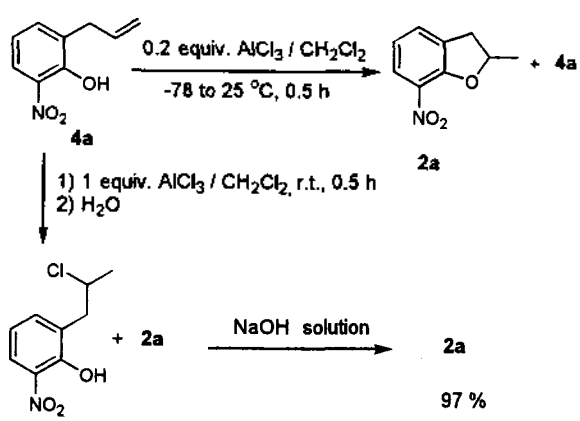
2,3-Dihydrobenzo[*b*]furan derivatives are very important intermediates for the preparation of pharmaceutical[1-3] and agricultural[4-6] agents. The 2,3-dihydrobenzo[*b*]furans were generally synthesized by acid-mediated cyclization such as strong acids,[7-12] $AlCl_3$,[13-14] $MgCl_2$,[1] $TiCl_4$,[15] and $ZnCl_2$.[16] The procedures were usually consisted of two steps: Claisen rearrangement of allyl phenyl ether to 2-allylphenol and the acid-mediated cyclization of the 2-allylphenol to 2,3-dihydrobenzo[*b*]furan. Recently, a convenient synthesis of 2,3-dihydrobenzo[*b*]furans with catalytic amount of $AlCl_3$[14] and I_2[17] was reported by Ryu and coworkers. However, the reactions of allyl phenyl ethers substituted with electron-withdrawing group provided low yields of desired benzo[*b*]furans. It was specifically noted that the cyclization of 2-allylnitrophenol did not give any desired product.[17] To investigate pharmaceutically useful benzo[*b*]furan analogues, we have been interested in synthesizing nitro substituted benzo[*b*]furans. Initially, we examined $AlCl_3$-mediated cyclization of various allyl 2-nitrophenyl ethers with 0.1-1.0 equiv. of $AlCl_3$. However, the reactions provided desired benzo[*b*]furans in low yields (<20%) and 2-nitrophenol which came from cleavage of allyl 2-nitrophenyl ether (Eq. 1).



(Eq. 1)

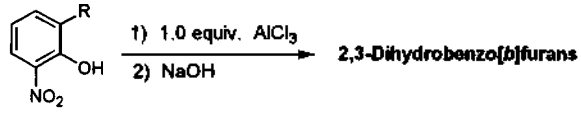
We employed 2-allyl-6-nitrophenol instead of allyl 2-nitrophenyl ether to improve the cyclization. The reaction of 2-allyl-6-nitrophenol, which was prepared by thermal Claisen rearrangement of allyl 2-nitrophenyl ether was treated with 0.1-0.2 equiv. of $AlCl_3$ at − 78 °C and followed by warming to room temperature over 0.5 h. The reaction gave less than 20% of benzo[*b*]furan and the starting material. We assumed that the reaction required 1.0 equiv. of $AlCl_3$ to cleave the tight intramolecular hydrogen bonding between phenolic hydrogen and oxygen of nitro group. The reaction using 1.0 equiv. of $AlCl_3$ provided a mixture of compounds **5** and **2a** (9 : 1) in quantitative yield. The treatment of the mixture of compouds **5** and **2a** with aqueous sodium hydroxide gave 7-nitro-2,3-dihydrobenzo[*b*]furan **2a** in 97% yield (Scheme 1).

With the optimized reaction conditions at hand, we in-



Scheme 1.

Table 1. $AlCl_3$/NaOH-mediated cyclization of 2-allyl-6-nitrophenols[a]



Entry	R	Product	Yield (%)
1	$-CH_2CH=CH_2$ **4a**	**2a**	97
2	$-CH_2C(CH_3)=CH_2$ **4b**	**2b**	90
3	$-CH(CH_3)CH=CH_2$ **4c**	**2c**	95
4[b]	$-CH_2CH=CHCH_3$ **4d**	**2d** + **6** (2 : 5)	84

[a] The reaction was carried out using 1.0 equiv. $AlCl_3/CH_2Cl_2$ at room temperature and worked up with 10% NaOH aqueous NaOH solution. [b] The products ratio was determined by ^1H NMR spectroscopy.

vestigated the $AlCl_3$/NaOH-mediated cyclization of several different 2-allyl-6-nitrophenols. The results are summarized in Table 1.

The substituent effect on allyl group was examined with methyl group. The reactions with 2-(2-methylallyl)-6-nitrophenol (**4b**) and 2-(1-methylallyl)-6-nitrophenol (**4c**) provided high yield of the desired products (entries 2 and 3). However, the reaction with 2-{(*E,Z*)-2-butenyl}-6-nitrophenol (**4d**) gave a mixture of 2-ethyl-7-nitro-2,3-dihydrobenzo[*b*]furan (**2d**) and 2-methyl-8-nitro-3,4-dihydrobenzopyran (**6**) in a ratio of 2 : 5. We also examined the 2-allyl-6-nitrophenol (**4a**) in a 0.5 mol scale. The reaction provided quantitative yield of 7-nitro-2-methyl-2,3-dihydrobenzo[*b*]furan (**2a**).

In conclusion, the $AlCl_3$/NaOH-mediated cyclization of various 2-allyl-6-nitrophenols provide 7-nitro-2,3-dihydrobenzo[*b*]furans in high yields under very mild reaction conditions and simple operations. The 7-nitro-2,3-dihydrobenzo [*b*]furans are very useful intermediates for the preperation of various biologically active compounds.

Experimental

The ^1H NMR spectra were obtained on a Varian Gemini 200 MHz. The GC-MS spectral data were obtained on a Shimazu QP 1000 mass spectrometer. Melting points were determined on MUL-TEM apparatus and were uncorrected. All chemicals were used directly as obtained from commercial sources unless otherwise noted.

2-Allyl-6-nitrophenol (4a). Allyl 2-nitrophenyl ether (24 g, 0.13 mol) was heated at 200 °C for 3 h with passing nitrogen. The reaction mixture was cooled and poured into 200 mL of cold water. The product was extracted with two 250 mL portions of diethyl ether. The etheral layer was dried over anhydrous $MgSO_4$ and concentrated. The 2-allyl-6-nitrophenol was obtained in 70% isolated yield after silica gel. column chromatography (hexane : ethyl acetate=9 : 1): yellow oil; ^1H NMR ($CDCl_3$) δ 3.47 (d, 2H, *J*=6.4 Hz), 5.05-5.14 (m, 2H), 5.95 (m, 1H), 6.90 (dd, 1H, *J*=8.4, 7.4 Hz), 7.44 (dd, 1H, *J*=7.4, 1.4 Hz), 7.91 (dd, 1H, *J*=8.4, 1.4 Hz), 10.93 (s, 1H); Mass m/e (%) 78 (17), 104 (19), 132 (83), 162 (100), 179 (53, M^+).

The following compounds (**4b-4d**) were prepared using the above procedure.

2-(2-Methylallyl)-6-nitrophenol (4b): yield 72%; mp 51-52 °C; ^1H NMR ($CDCl_3$) δ 1.73 (s, 3H), 3.41 (s, 3H), 4.66 (d, 1H, *J*=1.2 Hz), 4.84 (d, 1H, *J*=1.2 Hz), 6.91 (dd, 1H, *J*=8.6, 7.4 Hz), 7.45 (dd, 1H, *J*=7.4, 1.2 Hz), 7.99 (dd, 1H, *J*=8.6, 1.2 Hz), 10.93 (s, 1H); Mass m/e (%) 51 (100), 77 (67), 91 (48), 103 (39), 115 (54), 131 (81), 146 (66), 176 (73), 193 (51, M^+).

2-(1-Methylallyl)-6-nitrophenol (4c): yield 70%; yellow oil; ^1H NMR ($CDCl_3$) δ 1.37 (d, 3H, *J*=7.0 Hz), 4.03 (m, 1H), 5.07-5.17 (m, 2H), 6.02 (m, 1H), 6.94 (dd, 1H, *J*= 8.4, 7.4 Hz), 7.50 (dd, 1H, *J*=7.4, 1.2 Hz), 7.91 (dd, 1H, *J*= 8.4, 1.2 Hz), 11.06 (s, 1H); Mass m/e (%) 51 (90), 63 (63), 77 (79), 91 (55), 103 (52), 115 (51), 131 (100), 146 (72), 176 (72), 193 (16, M^+).

2-{(*E,Z*)-2-Butenyl}-6-nitrophenol (4d): yield 68%; yellow oil; ^1H NMR ($CDCl_3$) δ 1.69-1.76 (m, 3H), 3.40-3.43 (m, 2H), 5.65-5.62 (m, 2H), 6.92 (dd, 1H, *J*=8.6, 7.4 Hz), 7.47 (dd, 1H, *J*=7.4, 1.2 Hz), 7.99 (dd, 1H, *J*=8.6, 1.2 Hz), 11.10 (s, 1H); Mass m/e (%) 51 (79), 63 (39), 77 (66), 91 (42), 103 (38), 115 (45), 131 (100), 146 (55), 176 (76), 193 (27, M^+).

2-(2-Chloropropyl)-6-nitrophenol (5). 2-Allyl-6-nitrophenol (5.87 g, 32.8 mmol) was dissolved in 100 mL of dichloromethane and anhydrous $AlCl_3$ (4.36 g, 32.8 mmol) was slowly added with stirring. The reaction mixture was allowed to react for 0.5 h at room temperature. The reaction mixture was slowly added to 100 mL of precooled water. The product was extracted with two 250 mL portions of diethyl ether. The etheral layer was dried over anhydrous $MgSO_4$. The reaction mixture was filtered and concentrated. The compound **5** was obtained in 90% yield after silica gel column chromatography (hexane : ethyl acetate=9 : 1): yellow oil; ^1H NMR ($CDCl_3$) δ 1.61 (d, 3H, *J*=4.0 Hz), 3.05-3.24 (m, 2H), 4.44 (m, 1H), 6.99 (dd, 1H, *J*=8.6, 7.4 Hz), 7.54 (dd, 1H, *J*=7.4, 1.2 Hz), 8.07 (dd, 1H, *J*=8.6, 1.2 Hz), 10.99 (s, 1H); Mass m/e (%) 51 (16), 77 (16), 134 (16), 151 (100), 162 (28), 215 (10, M^+), 217 (3, M^++2).

2-Methyl-2,3-dihydrobenzo[*b*]furan (2a). 2-Allyl-6-nitrophenol (5.87 g, 32.8 mmol) was dissolved in 100 mL of dichloromethane and anhydrous $AlCl_3$ (4.36 g, 32.8 mmol) was slowly added with stirring. The reaction mixture was allowed to react for 0.5 h at room temperature. Precooled 100 mL of 10% sodium hydroxide solution was slowly added to the reaction mixture with ice cooling. The product was extracted with two 250 mL portions of diethyl ether. The etheral layer was dried over anhydrous $MgSO_4$. The reaction mixture was filtered and concentrated. The benzo[*b*] furan **2a** was obtained in 97% isolated yield after silica gel column chromatography (hexane : ethyl acetate=9 : 1): mp

65-66 °C; ^{1}H NMR ($CDCl_3$) δ 1.53 (d, 3H, *J*=6.3 Hz), 2.87 (dd, 1H, *J*=15.9, 7.2 Hz), 3.40 (dd, 1H, *J*=15.9, 8.4 Hz), 5.22 (m, 1H), 6.87 (dd, 1H, *J*=8.4, 7.2 Hz), 7.38 (dd, 1H, *J*=7.2, 1.2 Hz), 7.85 (dd, 1H, *J*=8.4, 1.2 Hz); Mass m/e (%) 77 (88), 103 (31), 117 (23), 132 (100), 162 (21), 179 (53, M^+).

The following compounds (**2b-2d** and **6**) were obtained using the above procedure.

2,2-Dimethyl-7-nitro-2,3-dihydrobenzo[*b*]furan (2b): yield 90%; mp 62-63 °C; ^{1}H NMR ($CDCl_3$) δ 1.55 (s, 6H), 3.07 (s, 2H), 6.85 (dd, 1H, *J*=8.4, 7.2 Hz), 7.36 (dd, 1H, *J*=7.2 Hz, 1.2 Hz), 7.86 (dd, 1H, *J*=8.4, 1.2 Hz); Mass m/e (%) 51 (82), 63 (30), 77 (58), 91 (32), 103 (29), 115 (43), 131 (100), 146 (72), 176 (69), 193 (48, M^+).

2,3-Dimethyl-7-nitro-2,3-dihydrobenzo[*b*]furan (2c): yield 95%; yellow oil; ^{1}H NMR ($CDCl_3$) δ 1.35 (d, 3H, *J*=7.0 Hz), 1.56 (d, 3H, *J*=6.6 Hz), 3.12 (m, 1H), 4.63 (m, 1H), 6.92 (dd, 1H, *J*=8.4, 7.2 Hz), 7.43 (dd, 1H, *J*=7.2, 1.2 Hz), 7.90 (dd, 1H, *J*=8.4, 1.2 Hz); Mass m/e (%) 51 (62), 63 (36), 77 (49), 91 (45), 103 (27), 115 (20), 131 (100), 146 (43), 176 (27), 193 (57, M^+).

2-Ethyl-7-nitro-2,3-dihydrobenzo[*b*]furan (2d): yield 24%; yellow oil; ^{1}H NMR ($CDCl_3$) δ 1.06 (t, 3H, *J*=7.4 Hz), 1.75-2.02 (m, 2H), 2.96 (dd, 1H, *J*=16.0, 7.4 Hz), 3.38 (dd, 1H, *J*=16.0, 9.2 Hz), 5.03 (m, 1H), 6.89 (dd, 1H, *J*=8.4, 7.2 Hz), 7.40 (dd, 1H, *J*=7.2, 1.2 Hz), 7.89 (dd, 1H, *J*=8.4, 1.2 Hz); Mass m/e (%) 131 (100), 146 (63), 176 (38), 193 (63, M^+).

2-Methyl-8-nitro-3,4-dihydro-2*H*-1-benzopyran (6): yield 60%; yellow oil; ^{1}H NMR ($CDCl_3$) δ 1.46 (d, 3H, *J*=6.4 Hz), 1.82 (m, 1H), 2.10 (m, 1H), 2.84-2.92 (m, 2H), 4.30 (m, 1H), 6.86 (dd, 1H, *J*=8.0, 7.2 Hz), 7.25 (dd, 1H, *J*=7.2, 0.8 Hz), 7.63 (dd, 1H, *J*=8.0, 0.8 Hz); Mass m/e (%) 105 (35), 130 (40), 131 (77), 135 (21), 152 (100), 176 (31) 193 (68, M^+).

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Palladium-Catalyzed Phosphonation of Heterocyclic Compounds Containing Nitrogen and Sulfur

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Although Arbuzov and Michaelis-Becker reactions are one of the most common methods for the formation of carbon-phosphorus bonds, they are not applicable to the formation of sp^2 hybridized carbon-phosphorus bonds.[1] Only a few methods to prepare arylphosphonates and vinylphosphonates have been reported.[2] Furthermore, these methods suffer from separation problems and the use of rather expensive reagents. T. Hirao reported the palladium-catalyzed sp^2 hybridized carbon-phosphorus bond formation.[3] However, the only one example of sp^2 hybridized carbon including heterocycles-phosphorus bond formation was repotred.[3] Recently we have studied the synthesis of heterocyclic aromatic phosphonate and their related derivatives in connection with our research program toward functionalization of heterocyclic aromatic compounds and studying the behavior of heterocyclic aromatic organophosphorus compounds with enzyme. Also, various phosphonates have been reported as having antagonistic and inhibitory effects.[1] In this paper, we wish to report palladium catalyzed phosphonation of heterocyclic aromatic compounds containing nitrogen and sulfur.

In order to access to the phosphonation, we began our stu-