Reactions of Nitroarenes with Secondary and Tertiary Carbanions Bearing Both a Leaving Group and Electron-Withdrawing Group: An Approach to Dihydronaphth[2,1-*c*]isoxazole *N*-oxides and Dihydroisoxazolo[4,3-*f*]quinoline *N*-oxides

Hiroshi Maruoka and Yukihiko Tomioka*

Faculty of Pharmaceutical Sciences, Fukuoka University,
8-19-1 Nanakuma, Jonan-ku, Fukuoka 814-0180, Japan

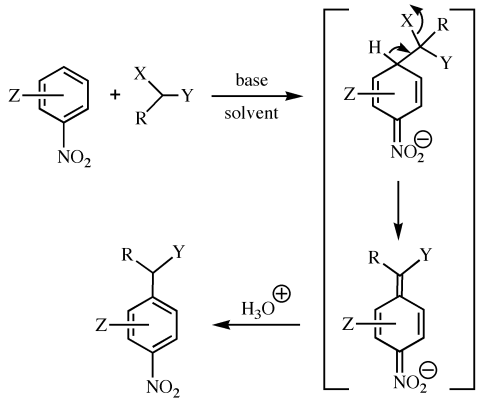
Received March 14, 2003

2-Nitronaphthalene (**1**) and 6-nitroquinoline (**2**) underwent direct cyclocondensation with secondary and tertiary carbanions derived from a methylene and methine group bearing both a leaving group and electron-withdrawing group (*e.g.*, methyl chloroacetate, ethyl chloroacetate, chloroacetonitrile, methyl 2-chloropropionate, ethyl 2-chloropropionate and 2-chloropropionitrile) in the sodium hydride/*N*,*N*-dimethylformamide system at low temperature, giving the corresponding dihydronaphth[2,1-*c*]isoxazole *N*-oxides **3** and dihydroisoxazolo[4,3-*f*]quinoline *N*-oxides **4**. On the other hand, nitroarenes **1** and **2** reacted with secondary carbanions in the sodium hydride/tetrahydrofuran system to yield the corresponding conventional vicarious nucleophilic substitution (VNS) products **5** and **6**.

J. Heterocyclic Chem., **40**, 1051 (2003).

Nitro compounds, especially aromatic nitro compounds, are used as intermediates in the synthesis of fine chemicals. Of course, they are very important for the preparation of dyes and explosives. The versatility of nitro compounds in organic synthesis is largely due to their easy availability and transformation into a variety of diverse functionalities [1-3]. Aromatic nitro compounds undergo nucleophilic aromatic substitutions with various nucleophiles. Nucleophilic aromatic substitution of hydrogen (NASH) process is an ideal process because NASH reactions generate functionalized aromatics without the need for halogenated materials. The vicarious nucleophilic substitution (VNS), pioneered by Makosza and coworkers, offers a selective mild method for the controlled substitution of hydrogen atoms of aromatic systems (Scheme 1) [4-8].

Scheme 1



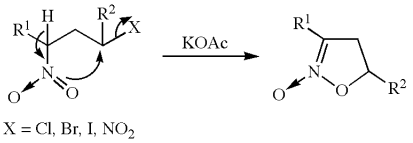
X = Cl, Br, OPh, SPh, *etc.*
Y = SO_2Ph, CN, CO_2Et, *etc.*
Z = Cl, OMe, CF_3, CN, *etc.*
R = H, Ph, alkyl
base: KOH, NaOH, *t*-BuOK, *etc.*
solvent: DMSO, DMF, THF, *etc.*

Recently, much attention has been paid to the development of new environmentally favorable routes for preparing commercially relevant chemical intermediates and products [9-14]. In this context, we have recently become interested in the development of new synthetic schemes for the construction of a series of 2,1-benzisoxazoles using applied VNS.

Available synthetic routes to 2-isoxazoline *N*-oxides proceed from either 3-halo-1-nitroalkanes or 1,3-dinitroalkanes. The methods were discovered and developed by Kohler and coworkers (Scheme 2) [15,16]. This reaction suggests the possibility that when aromatic nitro compound is treated with secondary or tertiary carbanion derived from a methylene or methine group bearing both a leaving group and electron-withdrawing group in the presence of an appropriate base/solvent system, the σ-adduct initially formed may undergo cyclization to furnish 2,1-benzisoxazole *N*-oxide. Isoxazoles and 2,1-benzisoxazoles are versatile compounds that have found application as intermediates and products in biological and pharmaceutical chemistry [17-22]. Several investigators have shown that aromatic nitro compounds react with nucleophiles to generate 2,1-benzisoxazoles [23-25]. We now report in this paper new approach to the one-pot synthesis of dihydronaphth[2,1-*c*]isoxazole *N*-oxides and dihydroisoxazolo[4,3-*f*]-quinoline *N*-oxides.

When a mixture of 2-nitronaphthalene (**1**) with methyl chloroacetate in the presence of sodium hydride in *N*,*N*-dimethylformamide was stirred at -10° for 4 hours, methyl 1,9b-dihydronaphth[2,1-*c*]isoxazole-1-carboxylate 3-oxide (**3a**) was obtained in 68% yield, and the VNS product was not observed with little or no creation. In contrast, in the sodium hydride/tetrahydrofuran system in stead of the sodium hydride/*N*,*N*-dimethylformamide system, the reaction of **1** with methyl chloroacetate gave the VNS

Scheme 2

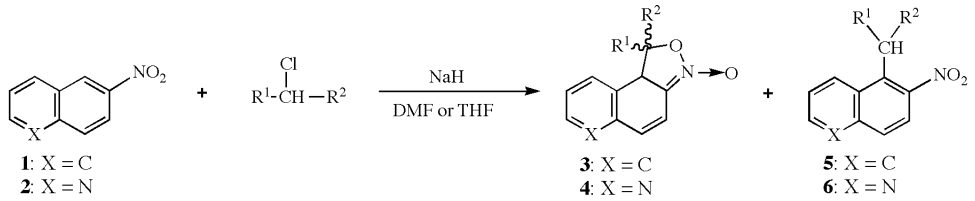


product **5a** [26] in 78% yield (Table 1). The ir spectrum of **3a** displays a band at 1738 cm^{-1} due to a carbonyl group, on the other hand, that of **5a** shows a band at 1735 cm^{-1}. The ^1H nmr spectrum of **3a** shows two singlets at δ 3.47 and 3.78 for a methyl group of a methoxy group, two doublets at δ 3.97 and 4.20 for a 1-methine group and two doublets at δ 1.57 and 3.48 for a 9b-methine group, whereas that of **5a** appears as a three-proton singlet at δ 3.73 for the methyl of a methoxy group and a two-proton singlet at δ 4.41 for a methylene group. Mass spectra and elemental analyses of **3a** and **5a** exhibit the same elemental composition $C_{13}H_{11}NO_4$ (see experimental section). These observations indicate that the structure of **3a** is obviously different from that of **5a**. Furthermore, **3a** exists as two diastereomers, which would probably be formed by an effect of the configuration of methoxycarbonyl group at the 1-position. On the basis of these results, **3a** was assigned as methyl 1,9b-dihydronaphth[2,1-*c*]isoxazole-1-carboxylate *N*-oxide, and the structure of **5a** was determined as the VNS product. Similarly, the reactions of **1** and 6-nitroquinoline (**2**) with secondary and tertiary carbanions in the sodium hydride/*N*,*N*-dimethylformamide system gave the corresponding dihydronaphth[2,1-*c*]isoxazole *N*-oxides **3b-f** and dihydroisoxazolo[4,3-*f*]quinoline *N*-oxides **4a-f** (Table 1). In these reactions, products **3b**, **3c**, **3f**, **4a-c** and **4e** were obtained as a mixture of two diastereomers as well as **3a** (see experimental section). While, in the sodium hydride/tetrahydrofuran system, **1** and **2** reacted with secondary carbanions to yield the corresponding VNS products **5b,c** and **6a-c**. In the case of tertiary carbanions, the VNS reaction was not observed and nitroarenes were recovered unchanged. Elemental analyses and spectral data of **3-6** are consistent with the assigned structures.

The formation of **3-6** can be explained in terms of Scheme 3. An addition of secondary or tertiary carbanions at positions 1 (compound **1**) and 5 (compound **2**) in the sodium hydride/*N*,*N*-dimethylformamide system gives the σ-adduct **A**, which undergoes intramolecular cyclization and dechlorination to form the 2,1-benzisoxazole *N*-oxides **3** and **4**. On the other hand, in the sodium hydride/tetrahydrofuran system, an elimination of hydrogen chloride from the σ-adduct **A** produces **B** which undergoes tautomerization to afford the VNS products **5** and **6**. Generally, the VNS reaction results in replacement of an aromatic hydrogen atom by a functionalised alkyl substituent. It is typically characterized by the addition to a nitroarene of a nucleophile bearing both an electron-withdrawing group and a leaving group at the reactive center [27,28]. In contrast, our results indicate that a new type of cyclocondensation occurs in the sodium hydride/*N*,*N*-dimethylformamide system and the VNS reaction dose not take place. To our knowledge, this type of cyclocondensation between nitroarenes and secondary or tertiary carbanions has not previously been reported. A new type of cyclocondensation, not the VNS reaction, depends on three factors:

Table 1

Reaction of **1** and **2** with Secondary and Tertiary Carbanions



1: X = C
2: X = N

3: X = C
4: X = N

5: X = C
6: X = N

Entry	X	R^1	R^2	Product	Yield (%)	Entry	X	R^1	R^2	Product	Yield (%)
1	C	H	CO_2Me	**3a**	68 [a]	10	N	H	CO_2Me	**4a**	16 [a]
2	C	H	CO_2Et	**3b**	88 [a]	11	N	H	CO_2Et	**4b**	51 [a]
3	C	H	CN	**3c**	27 [a]	12	N	H	CN	**4c**	12 [a]
4	C	Me	CO_2Me	**3d**	84 [a]	13	N	Me	CO_2Me	**4d**	83 [a]
5	C	Me	CO_2Et	**3e**	97 [a]	14	N	Me	CO_2Et	**4e**	90 [a]
6	C	Me	CN	**3f**	86 [a]	15	N	Me	CN	**4f**	74 [b]
7	C	H	CO_2Me	**5a** [26]	78 [b]	16	N	H	CO_2Me	**6a**	66 [b]
8	C	H	CO_2Et	**5b**	67 [b]	17	N	H	CO_2Et	**6b**	44 [b]
9	C	H	CN	**5c** [34]	38 [b]	18	N	H	CN	**6c** [7]	42 [b]

[a] solvent = DMF. [b] solvent = THF.

Scheme 3

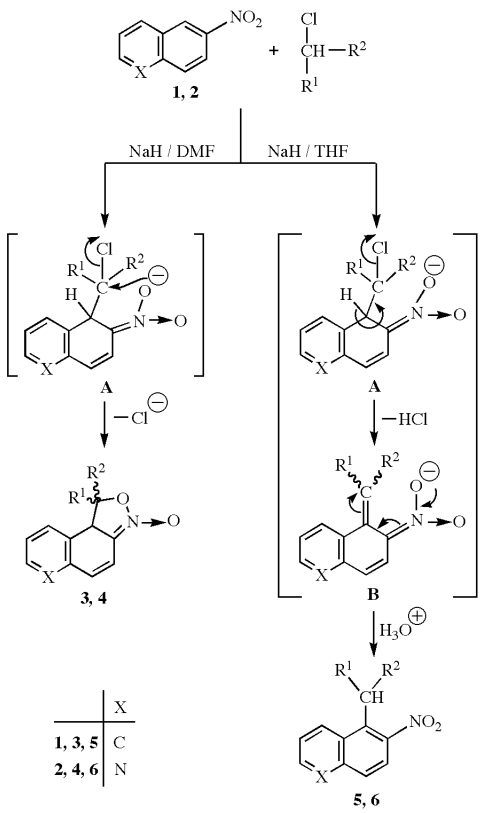
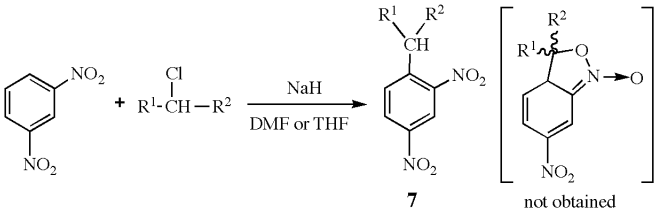


Table 2

Reaction of *m*-Dinitrobenzene with Secondary and Tertiary Carbanions



Entry	R^1	R^2	Product	Yield (%)
1	H	CO_2Me	**7a**	45 [a]
2	H	CO_2Et	**7b**	60 [a]
3	Me	CO_2Me	**7c**	46 [a]
4	Me	CO_2Et	**7d**	34 [a]
5	Me	CN	**7e**	64 [a]
6	H	CO_2Me	**7a**	23 [b]
7	H	CO_2Et	**7b**	22 [b]

[a] solvent = DMF. [b] solvent = THF.

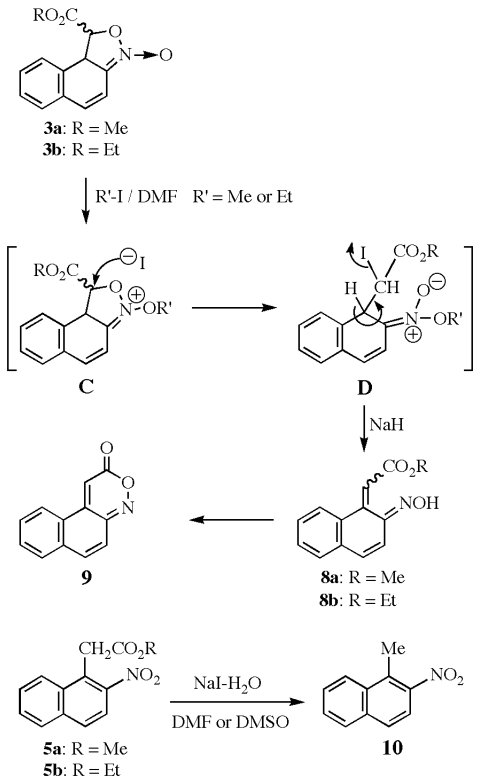
structure of the carbanions, structure of the nitroarenes and the reaction conditions.

We next tried the reaction of *m*-dinitrobenzene with secondary and tertiary carbanions in the sodium hydride/*N*,*N*-dimethylformamide system. In this case, the reaction afforded the VNS products **7a-e** and the desired 2,1-benzisoxazole *N*-oxides could not be obtained (Table 2). It is well known that several investigators [29-31] have reported the conventional VNS reaction of *m*-dinitrobenzene as the substrate and the VNS products are always obtained. In contrast, on the basis of our results, in bicyclic nitroarenes such as 2-nitronaphthalene and 6-nitroquinoline, the σ-adduct proceeds mainly cyclocondensation in the sodium hydride/*N*,*N*-dimethylformamide system. It makes us believe that the reaction mechanism is different from that of *m*-dinitrobenzene. The reason is not clear.

During our study of the synthesis of dihydronaphth-[2,1-*c*]isoxazole *N*-oxides, we found that compounds **3a,b** reacted with methyl (or ethyl) iodide in the presence of sodium hydride in *N*,*N*-dimethylformamide at room temperature to give **8a,b** and **9** (Scheme 4). This ring conversion probably proceeds through the intermediate **C**, which would undergoes ring opening and elimination of hydrogen iodide to give **8a,b**. Furthermore, cyclization of the (*Z*)-isomers of **8a,b** presumably affords the same 2*H*-naphth[2,1-*c*][1,2]oxazin-2-one (**9**). Finally, we have examined the decarboxylation of **5a,b** in order to confirm their structure. The reaction of **5a,b** with sodium iodide and water in *N*,*N*-dimethylformamide or dimethylsulfoxide according to the method of Gurjar *et al.* [32] proceeded smoothly to give 1-methyl-2-nitronaphthalene (**10**) [33].

In conclusion, we have developed a novel and efficient method for the construction of dihydronaphth[2,1-*c*]-

Scheme 4



isoxazole *N*-oxides and dihydroisoxazolo[4,3-*f*]quinoline *N*-oxides, which is based on the direct condensation of 2-nitronaphthalene and 6-nitroquinoline with secondary and tertiary carbanions in the sodium hydride/*N*,*N*-dimethylformamide system.

EXPERIMENTAL

All melting points are uncorrected. The ir spectra were recorded on a JASCO FT/IR-230 spectrometer. The ^{1}H nmr spectra were recorded on a JEOL JNM-A 500 spectrometer (500 MHz). Chemical shifts (δ) are reported in parts per million (ppm) relative to tetramethylsilane as internal standard. Positive FAB mass spectra were obtained on a JEOL JMS-HX 110 spectrometer. Elemental analyses were performed on a YANACO MT-6 CHN analyzer.

General Procedure for the Preparation of **3a-f** and **4a-f** from **1** and/or **2** and Secondary and/or Tertiary Carbanions.

To a solution of nitroarenes **1** (1.73 g, 10 mmoles) or **2** (1.74 g, 10 mmoles) and methyl chloroacetate (3.26 g, 30 mmoles), ethyl chloroacetate (3.68 g, 30 mmoles), chloroacetonitrile (2.27 g, 30 mmoles), methyl 2-chloropropionate (3.68 g, 30 mmoles), ethyl 2-chloropropionate (4.10 g, 30 mmoles) or 2-chloropropionitrile (2.69 g, 30 mmoles) in *N*,*N*-dimethylformamide (30 ml) was added 60% sodium hydride (1.20 g, 30 mmoles) at –10° (in the case of the preparation of **3a-c** and **4a-c**) or 0~5° (in the case of the preparation of **3d-f** and **4d-f**) with stirring. After the mixture was stirred at –10° for 4 hours (**3a-c** and **4a-c**) or 0~5° for 2 hours (**3d-f** and **4d-f**), cold water was added to the reaction mixture. The resulting mixture was extracted with chloroform. The extract was dried over anhydrous sodium sulfate and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel with chloroform as the eluent to afford **3a-f** and **4d-f**, or on alumina with chloroform as the eluent to yield **4a-c**. In the case of the preparation of **3c**, the first elution gave the starting material **1** (0.43 g, 25%).

Methyl 1,9b-Dihydronaphth[2,1-*c*]isoxazole-1-carboxylate 3-oxide (**3a**).

This compound was obtained as colorless needles (1.67 g, 68%), mp 88-89° (diethyl ether-petroleum ether); ir (potassium bromide): ν 1738 (C=O) cm^{-1}; ^{1}H nmr (deuteriochloroform): δ 1.57 (d, J = 6.7 Hz, 0.47H, 9b-H), 3.47 (s, 1.6H, CO_2Me), 3.48 (d, J = 11.3 Hz, 0.53H, 9b-H), 3.78 (s, 1.4H, CO_2Me), 3.97 (d, J = 11.3 Hz, 0.53H, 1-H), 4.20 (d, J = 6.7 Hz, 0.47H, 1-H), 6.63 (d, J = 10 Hz, 0.47H, 4-H), 6.67 (d, J = 10 Hz, 0.53H, 4-H), 6.72 (d, J = 10 Hz, 0.47H, 5-H), 6.79 (d, J = 10 Hz, 0.53H, 5-H), 7.25-7.37 (m, 3H, 6, 7 and 8-H), 7.46-7.48 (m, 0.53H, 9-H), 7.52-7.54 ppm (m, 0.47H, 9-H); ms: m/z 246 [M+H]$^+$.

Anal. Calcd. for $C_{13}H_{11}NO_4$: C, 63.67; H, 4.52; N, 5.71. Found: C, 63.66; H, 4.53; N, 5.63.

Ethyl 1,9b-Dihydronaphth[2,1-*c*]isoxazole-1-carboxylate 3-oxide (**3b**).

This compound was obtained as pale yellow oil (2.28 g, 88%), ir (neat): ν 1731 (C=O) cm^{-1}; ^{1}H nmr (deuteriochloroform): δ 0.99 (t, J = 7.3 Hz, 1.4H, $CO_2CH_2CH_3$), 1.28 (t, J = 7.3 Hz, 1.6H, $CO_2CH_2CH_3$), 1.55 (d, J = 6.7 Hz, 0.53H, 9b-H), 3.48 (d, J = 11.3 Hz, 0.47H, 9b-H), 3.86-3.93 (m, 0.93H, $CO_2CH_2CH_3$), 3.94 (d, J = 11.3 Hz, 0.47H, 1-H), 4.18 (d, J = 6.7 Hz, 0.53H, 1-H), 4.20-4.26 (m, 1.07H, $CO_2CH_2CH_3$), 6.62 (d, J = 10 Hz, 0.53H, 4-H), 6.68 (d, J = 10 Hz, 0.47H, 4-H), 6.72 (d, J = 10 Hz, 0.53H, 5-H), 6.76 (d, J = 10 Hz, 0.47H, 5-H), 7.25-7.36 (m, 3H, 6, 7 and 8-H), 7.46-7.48 (m, 0.47H, 9-H), 7.52-7.53 ppm (m, 0.53H, 9-H); ms: m/z 260 [M+H]$^+$.

Anal. Calcd. for $C_{14}H_{13}NO_4$: C, 64.86; H, 5.05; N, 5.40. Found: C, 64.84; H, 5.05; N, 5.46.

1,9b-Dihydronaphth[2,1-*c*]isoxazole-1-carbonitrile 3-oxide (**3c**).

This compound was obtained as colorless columns (0.57 g, 27%), mp 172-174° dec (acetone-petroleum ether); ir (potassium bromide): ν 2244 (C≡N) cm^{-1}; ^{1}H nmr (deuteriochloroform): δ 3.42 (d, J = 10.5 Hz, 1H, 9b-H), 4.08 and 4.09 (d, J = 10.5 Hz, 1H, 1-H), 6.76 and 6.77 (d, J = 10 Hz, 1H, 4-H), 6.95 (d, J = 10 Hz, 1H, 5-H), 7.39-7.43 (m, 3H, 6, 7 and 8-H), 7.51-7.53 ppm (m, 1H, 9-H); ms: m/z 212 [M$^+$].

Anal. Calcd. for $C_{12}H_8N_2O_2$: C, 67.92; H, 3.80; N, 13.20. Found: C, 67.87; H, 3.90; N, 13.14.

Methyl 1,9b-Dihydro-1-methylnaphth[2,1-*c*]isoxazole-1-carboxylate 3-oxide (**3d**).

This compound was obtained as colorless prisms (2.17 g, 84%), mp 111-113° (diethyl ether-petroleum ether); ir (potassium bromide): ν 1745 (C=O) cm^{-1}; ^{1}H nmr (deuteriochloroform): δ 0.87 (s, 3H, 1-Me), 3.79 (s, 3H, CO_2Me), 4.30 (s, 1H, 9b-H), 6.55 (d, J = 10 Hz, 1H, 4-H), 6.79 (d, J = 10 Hz, 1H, 5-H), 7.26-7.36 (m, 3H, 6, 7 and 8-H), 7.48-7.50 ppm (m, 1H, 9-H); ms: m/z 260 [M+H]$^+$.

Anal. Calcd. for $C_{14}H_{13}NO_4$: C, 64.86; H, 5.05; N, 5.40. Found: C, 64.85; H, 5.07; N, 5.37.

Ethyl 1,9b-Dihydro-1-methylnaphth[2,1-*c*]isoxazole-1-carboxylate 3-oxide (**3e**).

This compound was obtained as pale yellow oil (2.65 g, 97%), ir (neat): ν 1728 (C=O) cm^{-1}; ^{1}H nmr (deuteriochloroform): δ 0.87 (s, 3H, 1-Me), 1.29 (t, J = 7.3 Hz, 3H, $CO_2CH_2CH_3$), 4.24 (q, J = 7.3 Hz, 2H, $CO_2CH_2CH_3$), 4.29 (s, 1H, 9b-H), 6.56 (d, J = 10 Hz, 1H, 4-H), 6.78 (d, J = 10 Hz, 1H, 5-H), 7.28-7.36 (m, 3H, 6, 7 and 8-H), 7.48-7.50 ppm (m, 1H, 9-H); ms: m/z 274 [M+H]$^+$.

Anal. Calcd. for $C_{15}H_{15}NO_4 \bullet 0.1H_2O$: C, 65.92; H, 5.53; N, 5.13. Found: C, 65.48; H, 5.71; N, 4.90.

1,9b-Dihydro-1-methylnaphth[2,1-*c*]isoxazole-1-carbonitrile 3-oxide (**3f**).

This compound was obtained as colorless prisms (1.94 g, 86%), mp 103-105° (diethyl ether-petroleum ether); ir (potassium bromide): ν 2241 (C≡N) cm^{-1}; ^{1}H nmr (deuteriochloroform): δ 0.97 (s, 1.4H, 1-Me), 1.75 (s, 1.6H, 1-Me), 3.94 (s, 0.53H, 9b-H), 4.36 (s, 0.47H, 9b-H), 6.76 (d, J = 10 Hz, 0.47H, 4-H), 6.80 (d, J = 10 Hz, 0.53H, 4-H), 6.82 (d, J = 10 Hz, 0.47H, 5-H), 6.86 (d, J = 10 Hz, 0.53H, 5-H), 7.31-7.42 (m, 3H, 6, 7 and 8-H), 7.48-7.53 ppm (m, 1H, 9-H); ms: m/z 227 [M+H]$^+$.

Anal. Calcd. for $C_{13}H_{10}N_2O_2$: C, 69.02; H, 4.46; N, 12.38. Found: C, 69.02; H, 4.56; N, 12.36.

Methyl 1,9b-Dihydroisoxazolo[4,3-*f*]quinoline-1-carboxylate 3-oxide (**4a**).

This compound was obtained as colorless prisms (0.39 g, 16%), mp 94-96° (diethyl ether-petroleum ether); ir (potassium bromide): ν 1743 (C=O) cm^{-1}; ^{1}H nmr (deuteriochloroform): δ 1.64 (d, J = 6.7 Hz, 0.47H, 9b-H), 3.49 (s, 1.6H, CO_2Me), 3.54

(d, J = 11.3 Hz, 0.53H, 9b-H), 3.80 (s, 1.4H, CO_2Me), 3.98 (d, J = 11.3 Hz, 0.53H, 1-H), 4.21 (d, J = 6.7 Hz, 0.47H, 1-H), 6.87 (d, J = 10 Hz, 0.47H, 4-H), 6.96 (d, J = 10 Hz, 0.53H, 4-H), 7.00 (d, J = 10 Hz, 0.53H, 5-H), 7.04 (d, J = 10 Hz, 0.47H, 5-H), 7.25-7.29 (m, 1H, 8-H), 7.77-7.79 (m, 0.53H, 9-H), 7.83-7.85 (m, 0.47H, 9-H), 8.58-8.59 ppm (m, 1H, 7-H); ms: m/z 247 $[M+H]^+$.

Anal. Calcd. for $C_{12}H_{10}N_2O_4$: C, 58.54; H, 4.09; N, 11.38. Found: C, 58.61; H, 4.13; N, 11.27.

Ethyl 1,9b-Dihydroisoxazolo[4,3-*f*]quinoline-1-carboxylate 3-oxide (**4b**).

This compound was obtained as colorless needles (1.33 g, 51%), mp 64-66° (diethyl ether-petroleum ether); ir (potassium bromide): ν 1738 (C=O) cm^{-1}; ^1H nmr (deuteriochloroform): δ 1.01 (t, J = 7 Hz, 1.6H, $CO_2CH_2CH_3$), 1.29 (t, J = 7 Hz, 1.4H, $CO_2CH_2CH_3$), 1.62 (d, J = 6.7 Hz, 0.47H, 9b-H), 3.55 (d, J = 11.3 Hz, 0.53H, 9b-H), 3.88-3.95 (m, 1.07H, $CO_2CH_2CH_3$), 3.96 (d, J = 11.3 Hz, 0.53H, 1-H), 4.20 (d, J = 6.7 Hz, 0.47H, 1-H), 4.21-4.28 (m, 0.93H, $CO_2CH_2CH_3$), 6.86 (d, J = 10 Hz, 0.47H, 4-H), 6.98 (s, 1H, 4 and 5-H), 7.04 (d, J = 10 Hz, 0.53H, 5-H), 7.24-7.28 (m, 1H, 8-H), 7.77-7.79 (m, 0.53H, 9-H), 7.84-7.85 (m, 0.47H, 9-H), 8.57-8.59 ppm (m, 1H, 7-H); ms: m/z 261 $[M+H]^+$.

Anal. Calcd. for $C_{13}H_{12}N_2O_4$: C, 60.00; H, 4.65; N, 10.76. Found: C, 59.92; H, 4.63; N, 10.69.

1,9b-Dihydroisoxazolo[4,3-*f*]quinoline-1-carbonitrile 3-oxide (**4c**).

This compound was obtained as colorless needles (0.25 g, 12%), mp 162-164° dec (acetone-petroleum ether); ir (potassium bromide): ν 2245 (C≡N) cm^{-1}; ^1H nmr (deuteriochloroform): δ 3.50 (d, J = 10.7 Hz, 1H, 9b-H), 4.10 and 4.11 (d, J = 10.7 Hz, 1H, 1-H), 7.06 (d, J = 10.4 Hz, 1H, 4-H), 7.18 (d, J = 10.4 Hz, 1H, 5-H), 7.34 (dd, J = 5, 8 Hz, 1H, 8-H), 7.84 (dd, J = 1.5, 8 Hz, 1H, 9-H), 8.69 ppm (dd, J = 1.5, 5 Hz, 1H, 7-H); ms: m/z 214 $[M+H]^+$.

Anal. Calcd. for $C_{11}H_7N_3O_2$: C, 61.97; H, 3.31; N, 19.71. Found: C, 61.98; H, 3.41; N, 19.66.

Methyl 1,9b-Dihydro-1-methylisoxazolo[4,3-*f*]quinoline-1-carboxylate 3-oxide (**4d**).

This compound was obtained as colorless prisms (2.16 g, 83%), mp 92-93° (diethyl ether-petroleum ether); ir (potassium bromide): ν 1747 (C=O) cm^{-1}; ^1H nmr (deuteriochloroform): δ 0.92 (s, 3H, 1-Me), 3.81 (s, 3H, CO_2Me), 4.32 (s, 1H, 9b-H), 6.87 (d, J = 10 Hz, 1H, 4-H), 7.02 (d, J = 10 Hz, 1H, 5-H), 7.28 (dd, J = 4.5, 8 Hz, 1H, 8-H), 7.81-7.82 (m, 1H, 9-H), 8.59 ppm (dd, J = 1.5, 4.5 Hz, 1H, 7-H); ms: m/z 261 $[M+H]^+$.

Anal. Calcd. for $C_{13}H_{12}N_2O_4$: C, 60.00; H, 4.65; N, 10.76. Found: C, 60.03; H, 4.71; N, 10.57.

Ethyl 1,9b-Dihydro-1-methylisoxazolo[4,3-*f*]quinoline-1-carboxylate 3-oxide (**4e**).

This compound was obtained as pale orange oil (2.47 g, 90%), ir (neat): ν 1731 (C=O) cm^{-1}; ^1H nmr (deuteriochloroform): δ 0.92 (s, 3H, 1-Me), 1.30 (t, J = 7.3 Hz, 3H, $CO_2CH_2CH_3$), 4.26 and 4.27 (q, J = 7.3 Hz, 2H, $CO_2CH_2CH_3$), 4.31 (s, 1H, 9b-H), 6.87 and 6.88 (d, J = 10 Hz, 1H, 4-H), 7.02 (d, J = 10 Hz, 1H, 5-H), 7.28 (dd, J = 4.5, 8 Hz, 1H, 8-H), 7.82 (dd, J = 1.5, 8 Hz, 1H, 9-H), 8.59 ppm (dd, J = 1.5, 4.5 Hz, 1H, 7-H); ms: m/z 275 $[M+H]^+$.

Anal. Calcd. for $C_{14}H_{14}N_2O_4$: C, 61.31; H, 5.14; N, 10.21. Found: C, 61.41; H, 5.24; N, 10.14.

1,9b-Dihydro-1-methylisoxazolo[4,3-*f*]quinoline-1-carbonitrile 3-oxide (**4f**).

This compound was obtained as pale orange plates (1.68 g, 74%), mp 134-135° (acetone-petroleum ether); ir (potassium bromide): ν 2239 (C≡N) cm^{-1}; ^1H nmr (deuteriochloroform): δ 1.04 (s, 3H, 1-Me), 4.40 (s, 1H, 9b-H), 7.05 (d, J = 10 Hz, 1H, 4-H), 7.09 (d, J = 10 Hz, 1H, 5-H), 7.35 (dd, J = 5, 8 Hz, 1H, 8-H), 7.87 (dd, J = 1.5, 8 Hz, 1H, 9-H), 8.66 ppm (dd, J = 1.5, 5 Hz, 1H, 7-H); ms: m/z 228 $[M+H]^+$.

Anal. Calcd. for $C_{12}H_9N_3O_2$: C, 63.43; H, 3.99; N, 18.49. Found: C, 63.48; H, 4.07; N, 18.50.

General Procedure for the Preparation of VNS Products **5a-c** and **6a-c** from **1** and/or **2** and Secondary Carbanions.

To a solution of nitroarenes **1** (1.73 g, 10 mmoles) or **2** (1.74 g, 10 mmoles) and methyl chloroacetate (3.26 g, 30 mmoles), ethyl chloroacetate (3.68 g, 30 mmoles) or chloroacetonitrile (2.27 g, 30 mmoles) in tetrahydrofuran (30 ml) was added 60% sodium hydride (1.20 g, 30 mmoles) with stirring and ice-cooling. After the mixture was stirred at room temperature for 4 hours (in the case of the preparation of **5a-c** and **6a,c**) or refluxed for 1 hour (**6b**), cold water was added to the reaction mixture. The resulting mixture was extracted with ethyl acetate. The extract was dried over anhydrous sodium sulfate and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel with chloroform as the eluent to give **5a-c** and **6a-c**. In the case of the preparation of **5c**, the first elution gave the starting material **1** (0.18 g, 10%).

Methyl 2-Nitro-1-naphthaleneacetate (**5a**) [26].

This compound was obtained as yellow needles (1.91 g, 78%), mp 101-103° (acetone-petroleum ether); ir (potassium bromide): ν 1735 (C=O) cm^{-1}; ^1H nmr (deuteriochloroform): δ 3.73 (s, 3H, CO_2Me), 4.41 (s, 2H, CH_2CO_2Me), 7.65-7.69 (m, 2H, 6' and 7'-H), 7.89-7.97 (m, 3H, 4', 5' and 8'-H), 8.12-8.13 ppm (m, 1H, 3'-H); ms: m/z 246 $[M+H]^+$.

Anal. Calcd. for $C_{13}H_{11}NO_4$: C, 63.67; H, 4.52; N, 5.71. Found: C, 63.59; H, 4.54; N, 5.62.

Ethyl 2-Nitro-1-naphthaleneacetate (**5b**).

This compound was obtained as colorless needles (1.74 g, 67%), mp 88-90° (diethyl ether-petroleum ether); ir (potassium bromide): ν 1723 (C=O) cm^{-1}; ^1H nmr (deuteriochloroform): δ 1.25 (t, J = 7.3 Hz, 3H, $CO_2CH_2CH_3$), 4.20 (q, J = 7.3 Hz, 2H, $CO_2CH_2CH_3$), 4.40 (s, 2H, CH_2CO_2Et), 7.63-7.70 (m, 2H, 6' and 7'-H), 7.89-7.97 (m, 3H, 4', 5' and 8'-H), 8.12-8.16 ppm (m, 1H, 3'-H); ms: m/z 260 $[M+H]^+$.

Anal. Calcd. for $C_{14}H_{13}NO_4$: C, 64.86; H, 5.05; N, 5.40. Found: C, 64.87; H, 5.10; N, 5.35.

2-Nitro-1-naphthaleneacetonitrile (**5c**) [34].

This compound was obtained as colorless needless (0.81 g, 38%), mp 153-155° (acetone-petroleum ether); ir (potassium bromide): ν 2255 (C≡N) cm^{-1}; ^1H nmr (deuteriochloroform): δ 4.40 (s, 2H, CH_2CN), 7.73-7.82 (m, 2H, 6' and 7'-H), 7.97-8.00 (m, 3H, 4', 5' and 8'-H), 8.21-8.23 ppm (m, 1H, 3'-H); ms: m/z 213 $[M+H]^+$.

Anal. Calcd. for $C_{12}H_8N_2O_2$: C, 67.92; H, 3.80; N, 13.20. Found: C, 67.99; H, 3.94; N, 13.19.

Methyl 6-Nitro-5-quinolineacetate (**6a**).

This compound was obtained as colorless needless (1.63 g, 66%), mp 118-120° (acetone-petroleum ether); ir (potassium bromide): ν

1736 (C=O) cm^{-1}; ^1H nmr (deuteriochloroform): δ 3.74 (s, 3H, CO_2Me), 4.39 (s, 2H, CH_2CO_2Me), 7.60 (dd, J = 4.5, 8.5 Hz, 1H, 3'-H), 8.20 (s, 2H, 7' and 8'-H), 8.48 (dd, J = 1.5, 8.5 Hz, 1H, 4'-H), 9.07 ppm (dd, J = 1.5, 4.5 Hz, 1H, 2'-H); ms: m/z 247 $[M+H]^+$.

Anal. Calcd. for $C_{12}H_{10}N_2O_4$: C, 58.54; H, 4.09; N, 11.38. Found: C, 58.57; H, 4.09; N, 11.37.

Ethyl 6-Nitro-5-quinolineacetate (**6b**).

This compound was obtained as colorless needles (1.14 g, 44%), mp 148-150° (acetone-petroleum ether); ir (potassium bromide): ν 1722 (C=O) cm^{-1}; ^1H nmr (deuteriochloroform): δ 1.25 (t, J = 7.3 Hz, 3H, $CO_2CH_2CH_3$), 4.20 (q, J = 7.3 Hz, 2H, $CO_2CH_2CH_3$), 4.38 (s, 2H, CH_2CO_2Et), 7.60 (dd, J = 4.5, 8.5 Hz, 1H, 3'-H), 8.20 (s, 2H, 7' and 8'-H), 8.49 (dd, J = 1.5, 8.5 Hz, 1H, 4'-H), 9.07 ppm (dd, J = 1.5, 4.5 Hz, 1H, 2'-H); ms: m/z 261 $[M+H]^+$.

Anal. Calcd. for $C_{13}H_{12}N_2O_4$: C, 60.00; H, 4.65; N, 10.76. Found: C, 60.03; H, 4.61; N, 10.76.

6-Nitro-5-quinolineacetonitrile (**6c**) [7].

This compound was obtained as colorless scales (0.89 g, 42%), mp 168-170° dec (acetone-petroleum ether); ir (potassium bromide): ν 2251 (C≡N) cm^{-1}; ^1H nmr (deuteriochloroform): δ 4.41 (s, 2H, CH_2CN), 7.72 (dd, J = 4.5, 8 Hz, 1H, 3'-H), 8.24 (d, J = 9.2 Hz, 1H, 7'-H), 8.30 (d, J = 9.2 Hz, 1H, 8'-H), 8.56-8.59 (m, 1H, 4'-H), 9.15 ppm (dd, J = 1.5, 4.5 Hz, 1H, 2'-H); ms: m/z 214 $[M+H]^+$.

Anal. Calcd. for $C_{11}H_7N_3O_2$: C, 61.97; H, 3.31; N, 19.71. Found: C, 62.07; H, 3.40; N, 19.68.

General Procedure for the Preparation of VNS Products **7a-e** from *m*-Dinitrobenzene and Secondary and/or Tertiary Carbanions.

To a solution of *m*-dinitrobenzene (1.68 g, 10 mmoles) and methyl chloroacetate (3.26 g, 30 mmoles), ethyl chloroacetate (3.68 g, 30 mmoles), methyl 2-chloropropionate (3.68 g, 30 mmoles), ethyl 2-chloropropionate (4.10 g, 30 mmoles) or 2-chloropropionitrile (2.69 g, 30 mmoles) in *N*,*N*-dimethylformamide (30 ml) was added 60% sodium hydride (1.20 g, 30 mmoles) at –10° (in the case of the preparation of **7a,b**) or 0~5° (in the case of the preparation of **7c-e**) with stirring. After the mixture was stirred at –10° for 4 hours (**7a,b**) or 0~5° for 4 hours (**7c-e**), cold water was added to the reaction mixture. The resulting mixture was extracted with chloroform. After work-up as described for the preparation of VNS products **5a-c** and **6a-c**, compounds **7a-e** were obtained.

Methyl 2,4-Dinitrobenzeneacetate (**7a**).

This compound was obtained as colorless needles (1.09 g, 45%, in the case of the use of *N*,*N*-dimethylformamide; 0.56 g, 23%, in the case of the use of tetrahydrofuran), mp 42-44° (diethyl ether-petroleum ether); ir (potassium bromide): ν 1739 (C=O) cm^{-1}; ^1H nmr (deuteriochloroform): δ 3.74 (s, 3H, CO_2Me), 4.15 (s, 2H, CH_2CO_2Me), 7.61 (d, J = 8.5 Hz, 1H, 6'-H), 8.44 (dd, J = 2.4, 8.5 Hz, 1H, 5'-H), 8.94 ppm (d, J = 2.4 Hz, 1H, 3'-H); ms: m/z 241 $[M+H]^+$.

Anal. Calcd. for $C_9H_8N_2O_6$: C, 45.01; H, 3.36; N, 11.66. Found: C, 44.86; H, 3.32; N, 11.65.

Ethyl 2,4-Dinitrobenzeneacetate (**7b**).

This compound was obtained as pale yellow oil (1.53 g, 60%, in the case of the use of *N*,*N*-dimethylformamide; 0.56 g, 22%, in the case of the use of tetrahydrofuran); ir (neat): ν 1732 (C=O) cm^{-1}; ^1H nmr (deuteriochloroform): δ 1.26 (t, J = 7.3 Hz, 3H, $CO_2CH_2CH_3$), 4.14 (s, 2H, CH_2CO_2Et), 4.19 (q, J = 7.3 Hz, 2H, $CO_2CH_2CH_3$), 7.60 (d, J = 8.5 Hz, 1H, 6'-H), 8.43 (dd, J = 2.4, 8.5 Hz, 1H, 5'-H), 8.94 ppm (d, J = 2.4 Hz, 1H, 3'-H); ms: m/z 255 $[M+H]^+$.

Anal. Calcd. for $C_{10}H_{10}N_2O_6$: C, 47.25; H, 3.97; N, 11.02. Found: C, 47.21; H, 3.93; N, 10.93.

Methyl α-Methyl-2,4-dinitrobenzeneacetate (**7c**).

This compound was obtained as colorless needles (1.17 g, 46%), mp 54-55° (diethyl ether-petroleum ether); ir (potassium bromide): ν 1730 (C=O) cm^{-1}; ^1H nmr (deuteriochloroform): δ 1.66 (d, J = 7 Hz, 3H, 3-Me), 3.70 (s, 3H, CO_2Me), 4.42 (q, J = 7 Hz, 1H, 2-H), 7.74 (d, J = 8.5 Hz, 1H, 6'-H), 8.44 (dd, J = 2.4, 8.5 Hz, 1H, 5'-H), 8.78 ppm (d, J = 2.4 Hz, 1H, 3'-H); ms: m/z 255 $[M+H]^+$.

Anal. Calcd. for $C_{10}H_{10}N_2O_6$: C, 47.25; H, 3.97; N, 11.02. Found: C, 47.22; H, 4.05; N, 10.96.

Ethyl α-Methyl-2,4-dinitrobenzeneacetate (**7d**).

This compound was obtained as pale yellow needles (0.91 g, 34%), mp 36-37° (diethyl ether-petroleum ether); ir (potassium bromide): ν 1732 (C=O) cm^{-1}; ^1H nmr (deuteriochloroform): δ 1.21 (t, J = 7.3 Hz, 3H, $CO_2CH_2CH_3$), 1.66 (d, J = 7 Hz, 3H, 3-Me), 4.13-4.18 (m, 2H, $CO_2CH_2CH_3$), 4.40 (q, J = 7 Hz, 1H, 2-H), 7.74 (d, J = 8.5 Hz, 1H, 6'-H), 8.43 (dd, J = 2.4, 8.5 Hz, 1H, 5'-H), 8.78 ppm (d, J = 2.4 Hz, 1H, 3'-H); ms: m/z 269 $[M+H]^+$.

Anal. Calcd. for $C_{11}H_{12}N_2O_6$: C, 49.26; H, 4.51; N, 10.44. Found: C, 49.30; H, 4.54; N, 10.21.

α-Methyl-2,4-dinitrobenzeneacetonitrile (**7e**).

This compound was obtained as pale yellow needles (1.41 g, 64%), mp 108-110° (acetone-petroleum ether); ir (potassium bromide): ν 2248 (C≡N) cm^{-1}; ^1H nmr (deuteriochloroform): δ 1.77 (d, J = 7 Hz, 3H, 3-Me), 4.85 (q, J = 7 Hz, 1H, 2-H), 8.07 (d, J = 8.5 Hz, 1H, 6'-H), 8.56 (dd, J = 2.4, 8.5 Hz, 1H, 5'-H), 8.90 ppm (d, J = 2.4 Hz, 1H, 3'-H); ms: m/z 222 $[M+H]^+$.

Anal. Calcd. for $C_9H_7N_3O_4$: C, 48.87; H, 3.19; N, 19.00. Found: C, 48.97; H, 3.33; N, 18.98.

The Preparation of **8a,b** and **9** from **3a,b**.

To a solution of **3a** (1.23 g, 5 mmoles) or **3b** (1.30 g, 5 mmoles) and methyl iodide (2.13 g, 15 mmoles, in the case of the reaction of **3a**) or ethyl iodide (2.34 g, 15 mmoles, in the case of the reaction of **3b**) in *N*,*N*-dimethylformamide (10 ml) was added 60% sodium hydride (0.20 g, 5 mmoles) with stirring and ice-cooling. After the mixture was stirred at room temperature overnight, a saturated aqueous sodium thiosulfate (30 ml) was added to the reaction mixture with stirring and ice-cooling. The resulting mixture was extracted with chloroform. The extract was dried over anhydrous sodium sulfate and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel with chloroform as the eluent to give the same **9** [from **3a**: 0.35 g (36%), from **3b**: 0.30 g (30%)]. Further the elution afforded **8a** [from **3a**: 0.22 g (19%)] and **8b** [from **3b**: 0.23 g (19%)].

Methyl (*E*/*Z*)-2-(2-Hydroxyimino-1-naphthylidene)acetate (**8a**)

This compound was obtained as yellow needles, mp 164-166° dec (acetone-petroleum ether); ir (potassium bromide): ν 3261 (OH), 1715 (C=O) cm^{-1}; ^1H nmr (deuteriochloroform): δ 3.87 (s,

3H, CO_2Me), 6.74 (d, J = 12.5 Hz, 1H, 3'-H), 7.06 (d, J = 12.5 Hz, 1H, 4'-H), 7.30-7.39 (m, 4H, 5', 6', 7' and 8'-H), 7.36 (s, 1H, 2-H), 9.36 ppm (br s, 1H, OH); ms: m/z 230 $[M+H]^+$.

Anal. Calcd. for $C_{13}H_{11}NO_3$: C, 68.11; H, 4.84; N, 6.11. Found: C, 68.14; H, 4.94; N, 5.92.

Ethyl (*E*/*Z*)-2-(2-Hydroxyimino-1-naphthylidene)acetate (**8b**)

This compound was obtained as pale orange plates, mp 161-163° dec (acetone-petroleum ether); ir (potassium bromide): ν 3267 (OH), 1712 (C=O) cm^{-1}; ^1H nmr (deuteriochloroform): δ 1.36 (t, J = 7.3 Hz, 3H, $CO_2CH_2CH_3$), 4.34 (q, J = 7.3 Hz, 2H, $CO_2CH_2CH_3$), 6.73 (d, J = 12.5 Hz, 1H, 3'-H), 7.06 (d, J = 12.5 Hz, 1H, 4'-H), 7.37 (s, 1H, 2-H), 7.30-7.39 (m, 4H, 5', 6', 7' and 8'-H), 9.25 ppm (br s, 1H, OH); ms: m/z 244 $[M+H]^+$.

Anal. Calcd. for $C_{14}H_{13}NO_3$: C, 69.12; H, 5.39; N, 5.76. Found: C, 69.09; H, 5.42; N, 5.63.

2*H*-Naphth[2,1-*c*][1,2]oxazin-2-one (**9**).

This compound was obtained as orange needles, mp 222-224° dec (acetone-petroleum ether); ir (potassium bromide): ν 1756 (C=O), 1655 (C=C) cm^{-1}; ^1H nmr (DMSO-d_6): δ 6.98 (d, J = 12.2 Hz, 1H, 5-H), 7.40 (d, J = 12.2 Hz, 1H, 6-H), 7.69-7.72 (m, 1H, 9-H), 7.82-7.83 (m, 2H, 7 and 8-H), 8.15 (d, J = 7.6 Hz, 1H, 10-H), 8.26 ppm (s, 1H, 1-H); ms: m/z 198 $[M+H]^+$.

Anal. Calcd. for $C_{12}H_7NO_2$: C, 73.09; H, 3.58; N, 7.10. Found: C, 73.04; H, 3.63; N, 7.00.

The Preparation of **10** from **5a** or **5b**.

A mixture of **5a** (1.23 g, 5 mmoles) or **5b** (1.30 g, 5 mmoles) and sodium iodide (3.00 g, 20 mmoles) in *N*,*N*-dimethylformamide (10 ml, in the case of the reaction of **5a**) or dimethylsulfoxide (10 ml, in the case of the reaction of **5b**) and water (1 ml) was refluxed for 8 hours (**5a**) or 20 hours (**5b**), and then cold water was added to the reaction mixture. The resulting mixture was extracted with chloroform. The extract was dried over anhydrous sodium sulfate and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel with chloroform as the eluent to give 1-methyl-2-nitronaphthalene (**10**) [32] as yellow needles [from **5a**: 0.68 g (73%), from **5b**: 0.24 g (26%)], mp 57-59° (diethyl ether-petroleum ether); ^1H nmr (deuteriochloroform): δ 2.83 (s, 3H, 1-Me), 7.63-7.67 (m, 2H, 6 and 7-H), 7.78 (s, 2H, 4 and 5-H), 7.88-7.90 (m, 1H, 8-H), 8.18-8.20 ppm (m, 1H, 3-H); ms: m/z 188 $[M+H]^+$.

Anal. Calcd. for $C_{11}H_9NO_2$: C, 70.58; H, 4.85; N, 7.48. Found: C, 70.61; H, 4.90; N, 7.35.

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