HETEROCYCLES, Vol. 53, No. 5, 2000, pp. 1075 - 1084, Received, 4th February, 2000

PREPARATION OF 2-SUBSTITUTED NAPHTH[2,3-*d*]OXAZOLE-4,9-DIONES *VIA* A RADICAL CHAIN PROCESS

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Abstract - A novel series of ethylenic naphth[2,3-*d*]oxazole-4,9-diones was synthesized *via* an $S_{RN}1$ mechanism from the 2-chloromethylnaphth[2,3-*d*]oxazole-4,9-dione. This mechanism was confirmed by the inhibitory effects of the use of dark, bubbling oxygen, cupric chloride, *p*-dinitrobenzene and TEMPO.

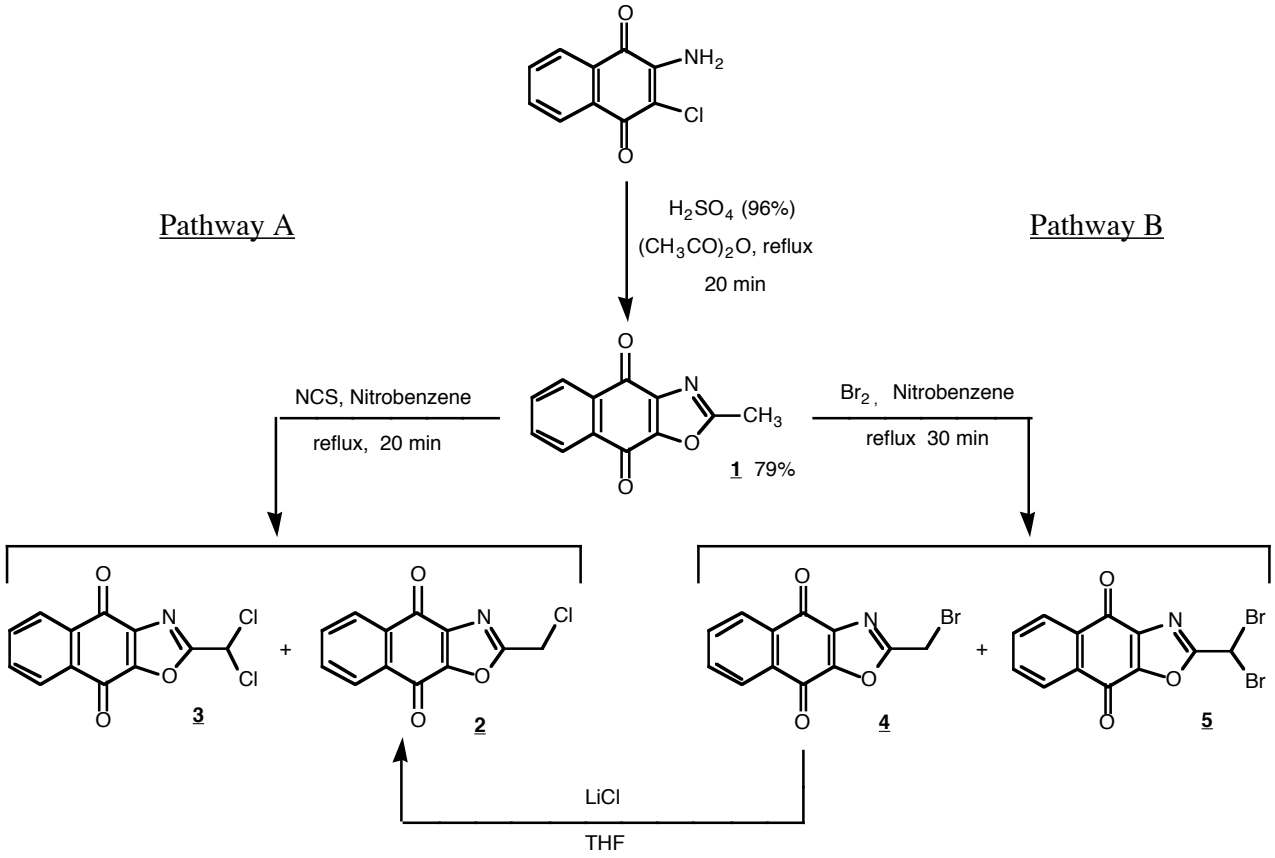
Since the discovery of naturally occurring heterocyclic quinones having potentially important biological properties,[1] synthetic work designed to produce the heterocyclic quinone system has been encouraged in an efficient manner in order to effect a total synthesis of the naturally occurring quinone or to produce a series of analogues of bioactive compounds for subsequent structure-activity relationships.[2] This is well exemplified by the case of the antitumor antibiotic, mitomycin,[3] and by the idea of bioreductive activation of certain quinones.[4] So, several quinones, where the naphthoquinone and a heterocyclic (thiophene,[5] furan,[6] imidazole[7] or oxazole[8]) system are coplanar, have recently been investigated as antitumour agents. In connection with our program directed toward the development of novel synthetic quinone congeners as anticancer agents,[9] we report herein a new preparative method to produce new oxazoloquinones.

In order to demonstrate that a naphthoxazole-quinone is able to react by an $S_{RN}1$ mechanism, we have synthesized the 2-chloromethylnaphth[2,3-*d*]oxazole-4,9-dione (**2**) and studied its reactivity with 2-nitropropane anion (**6a**).

First, we tried to obtain **2** in a one pot synthesis, modifying several protocols developed to prepare the corresponding 2-methyl derivative.[10-12] However, all attempts failed to get the required chloride (**2**) in good yields. Thus, we have used the Fries procedure[12] to prepare the 2-methylnaphth[2,3-*d*]oxazole-4,9-dione (**1**) followed by halogenation of the 2-methyl group. Two different routes leading to **2** are shown in Scheme 1. In pathway A, the *N*-chlorosuccinimide (NCS) free radical chlorination has been performed in nitrobenzene

instead of carbon tetrachloride, the classical solvent used for this reaction,[13] owing to the very low solubility of **1** in such a solvent.

Scheme 1



The reaction led to a mixture of **2** (43%) and **3** (25%) in addition to unreacted starting material. These two chlorides were very hard to separate by chromatography because of their low solubility in classical solvents. For this reason, we followed another route in pathway B, in order to prepare **2** with more selectivity. Thus **1** was brominated with bromine in refluxed nitrobenzene under irradiation.

Table 1

Influence of the experimental conditions in the reaction of **1** with bromine

Entry	Br_2 (mol. equiv.)	Time	Nitrobenzene[a]	**1** Yield (%)	**4** Yield (%)	**5** Yield (%)
1	2	3 h	40 mL	17	38	10
2	1.5	6 h	40 mL	15	41	12
3	2	20 min	20 mL	19	54	trace
4	2	20 min	10 mL	17	53	trace

[a]Nitrobenzene quantity per gramme of **1**.

For Entry 1 (Table 1), a mixture of 4, 5 and unreacted starting material was obtained. But after the optimization of this reaction, modifying bromine concentration, reaction time and nitrobenzene quantity, only a trace amount of 5 was produced and this was easily eliminated during the work-up of the reaction product (Table 1). Treatment of 4 with lithium chloride gave the required chloride (2) in 92% yield (Scheme 1).

In order to study the reactivity of **2** with the 2-nitropropane anion (**6a**) (Scheme 2), various reaction conditions were performed, as shown in Table 2, and only 2-isopropylidenemethylnaphth[2,3-*d*]oxazole-4,9-dione (**8a**) was isolated.

Scheme 2

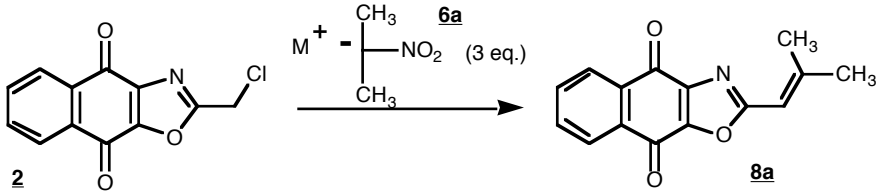


Table 2

Influence of the experimental conditions in the reaction of **2** with **6a**[a]

Entry	M^+	Solvent	Time	Scavenger (mol. equiv.)	**8a** Yield (%)
1	NBu_4	CH_2Cl_2/H_2O[b]	24 h	-	37
2	Li	DMF	15 min	-	Degradation products
3	Li	DMF	4 h	-	Degradation products
4	Li	DMSO	24 h	-	75
5	Li	DMSO	24 h	$CuCl_2$, $2H_2O$ (0.1 eq.)	19
6	Li	DMSO	24 h	$CuCl_2$, $2H_2O$ (1 eq.)	9
7	Li	DMSO	24 h	*p*-$NO_2C_6H_4NO_2$ (0.1 eq.)	14
8	Li	DMSO	24 h	*p*- $NO_2C_6H_4NO_2$ (1 eq.)	0
9	Li	DMSO	24 h	TEMPO (0.1 eq.)	0
10	Li	DMSO	24 h	O_2 (bubbling)	5
11	Li	DMSO	24 h	dark	7
12	Li	DMSO	24 h	O_2 (bubbling) + dark	3

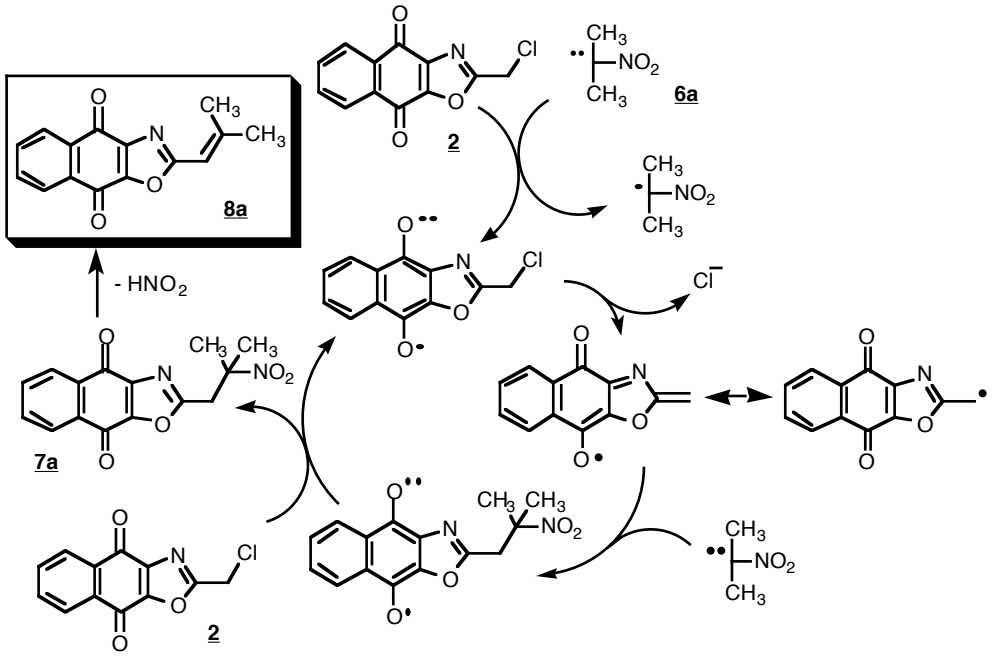
[a]All reactions were performed with 3 equivalents of **6a**, under nitrogen and irradiation with two 60 W tungsten lamps. [b]Phase-transfer conditions with 40% $N(C_4H_9)_4OH$ in water.

The best *C*-alkylation yield was obtained under Kornblum conditions[14,15] (Entry 4), comparatively to the Norris procedure[16] (Entry 1). This was probably due to the solubility of **2** which was very low in dichloromethane and dimethylformamide (DMF), higher in dimethyl sulfoxide (DMSO). As previously reported in heterocyclic series[17] or in quinone series,[18] the use of an excess of the anion gave better yields in *C*-alkylation products formed by an $S_{RN}1$ mechanism. With **2**, the best yield of the alkene (**8a**) (85%) was obtained when 3 equivalents of the anion (**6a**) were used. The best experimental conditions (Entry 4) were used to perform the classical inhibition experiments,[19] such as the use of dark, electron trapping and radical scavenging. The formation of **8a** strongly decreased when cupric chloride or catalytic quantities of *p*-dinitrobenzene (*p*-DNB) was added to the reaction mixture (Entries 5-7). The same result was observed

when the reaction was performed under bubbling oxygen or/and in the dark (Entries 10-12). The use of catalytic quantities of 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) (Entry 9) or stoichiometric quantity of *p*-DNB (Entry 8) completely inhibited the chain reaction process.

All the results of these inhibition experiments provide a good evidence for assigning the following $S_{RN}1$ mechanism (Scheme 3) for the formation of **8a**.

Scheme 3



The ethylenic derivative (**8a**) was formed *via* the *C*-alkylation product (**7a**) by base promoted nitrous acid elimination which occurred spontaneously in the reaction mixture since we have never been able to isolate **7** in this series. In order to prepare a novel naphthoxazole-quinone series with a potential cytotoxic activity, we have prepared various aliphatic, cyclic and heterocyclic lithium salts from the corresponding amines, as previously described.[20,21] Derivative (**2**) was treated by 3 equivalents of the anion (**6b-j**), in the experimental conditions of Entry 4 (Scheme 4): stirring at room temperature during 24 h in degassed DMSO, under nitrogen and irradiation with two 60 W tungsten lamps. The corresponding ethylenic derivatives (**8b-j**) were purified in good yields, as shown in Table 3. When the ethylenic derivative was unsymmetrical, the *E* isomer was the main product. This selectivity may be explained by favored conformations of the *C*-alkylated derivative and was optimal with the use of the 1-nitro-1,2,3,4-tetrahydronaphthalene salt (**6h**) because only the *E* isomer was isolated. This was probably due to a steric hindrance between the oxazoloquinone and the 1,2,3,4-tetrahydronaphthalene rings. The same observation was already described in a nitroisoquinoline series[22] with the use of the 1-nitroindane lithium salt.

Scheme 4

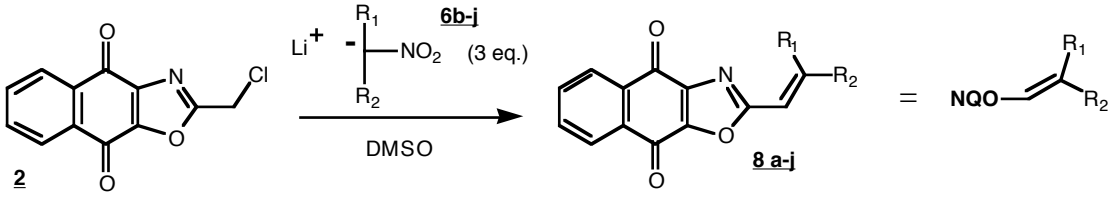
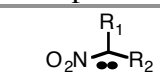
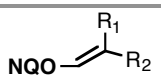
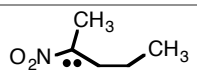
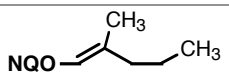
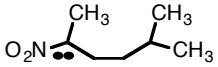
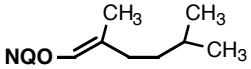
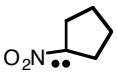
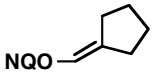
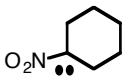
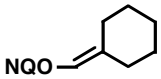
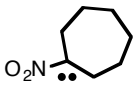
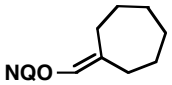
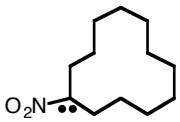
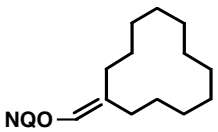
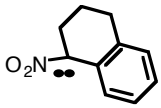
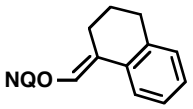
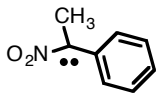
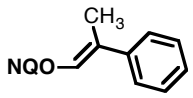
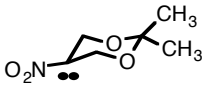
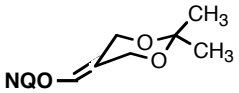


Table 3

Ethylenic compounds (**8b-j**) synthesized by $S_{RN}1$ reactions of **2** with various nitronate anions

Anion		Entry	Compound		**8** Yield (%)	*E* / *Z* ratio
6b		1	**8b**		71	4 / 1
6c		2	**8c**		74	4 / 1
6d		3	**8d**		58	-
6e		4	**8e**		66	-
6f		5	**8f**		71	-
6g		6	**8g**		65	-
6h		7	**8h**		70	1 / 0
6i		8	**8i**		58	4 / 1
6j		9	**8j**		60	-

In conclusion, the versatile $S_{RN}1$ mechanism offers a promising tool for the synthesis, in mild operating conditions, of new naphth[2,3-*d*]oxazole-4,9-diones, bearing a trisubstituted double bond at the 2-position, which are difficult to obtain by classical procedures.

ACKNOWLEDGEMENTS

We are grateful to the Centre National de la Recherche Scientifique for financial support. We express our thanks to Gilles Lanzada for his technical collaboration.

EXPERIMENTAL

Melting points were determined on a Büchi capillary melting point apparatus and are uncorrected. Elemental analyses were performed by the Centre de Microanalyses of the University of Aix-Marseille 3. ^{1}H NMR spectra were determined on a Bruker ARX 200 spectrometer. The ^{1}H chemical shifts are reported as parts per million downfield from tetramethylsilane (Me_4Si). Absorptions are reported with the following

notations: s, singlet; d, doublet; t, triplet; q, quartet; m, a more complex multiplet or overlapping multiplets. The following adsorbent was used for column chromatography: silica gel 60 (Merck, particle size 0.063-0.200 mm, 70-230 mesh ASTM).

2-Methylnaphth[2,3-*d*]oxazole-4,9-dione (1)

96% Sulfuric acid (0.5 mL) was added to a solution of 2-amino-3-chloro-1,4-naphthoquinone (1 g, 4.8 mmol) in acetic anhydride (10 mL). The reaction mixture was refluxed during 30 min. The starting orange solution turned to the black. After cooling at rt, the brown precipitate obtained was collected by filtration and then recrystallized from ethanol to give 0.87 g (79%) of yellow solid. **1**, mp 319-320 °C (mp 318-319 °C lit.,[10]), ^{1}H NMR ($CDCl_3$) δ 2.77 (s, 3H, CH_3); 7.72-7.77 (m, 2H, H_6, H_7); 8.14-8.21 (m, 2H, H_5, H_8).

2-Chloromethylnaphth[2,3-*d*]oxazole-4,9-dione (2)

Pathway A: *N*-Chlorosuccinimide (2.16 g, 14 mmol) was added to a solution of **1** (1 g, 4.7 mmol) in refluxing nitrobenzene (50 mL). The reaction mixture was refluxed during 20 min under irradiation with two 60 W tungsten lamps. After cooling at rt, the yellow precipitate was filtered and washed with ethanol. Chromatography on a silica gel column with dichloromethane as eluent gave a mixture of **1** (0.06 g, 6%), **2** (0.50 g, 43%) and 2-dichloromethylnaphth[2,3-*d*]oxazole-4,9-dione (**3**) (0.33 g, 25%). **2**, yellow solid, mp 272 °C (ethyl acetate), ^{1}H NMR ($CDCl_3$) δ 4.70 (s, 2H, CH_2Cl); 7.72-7.77 (m, 2H, H_6, H_7); 8.14-8.21 (m, 2H, H_5, H_8), Anal. Calcd for $C_{12}H_6NO_3Cl$: C, 58.20; H, 2.44; N, 5.66; Cl, 14.3. Found: C, 58.21; H, 2.50; N, 5.58; Cl, 14.3. **3**, yellow solid, mp 224 °C (ethyl acetate), ^{1}H NMR ($CDCl_3$) δ 6.78 (s, 1H, $CHCl_2$); 7.74-7.81 (m, 2H, H_6, H_7); 8.16-8.23 (m, 2H, H_5, H_8); Anal. Calcd for $C_{12}H_5NO_3Cl_2$: C, 51.10; H, 1.78; N, 4.96; Cl, 25.1. Found: C, 51.07; H, 1.76; N, 4.93; Cl, 25.0.

Pathway B: Bromine (0.48 mL, 9.38 mmol) was added dropwise to a solution of **1** (2 g, 9.38 mmol) in refluxed nitrobenzene (20 mL). The mixture was refluxed during 20 min under irradiation with two 60 W tungsten lamps. After cooling at rt, the precipitate was filtered and washed with petroleum ether. The residue was purified by chromatography on a silica gel column eluting with dichloromethane to give a mixture of **1** (0.34 g, 17% yield), 2-bromomethylnaphth[2,3-*d*]oxazole-4,9-dione (**4**) (1.45 g, 53%) and traces of 2-dibromomethylnaphth[2,3-*d*]oxazole-4,9-dione (**5**). **4**, yellow crystals, mp 261 °C (isopropanol), ^{1}H NMR ($CDCl_3$) δ 4.60 (s, 2H, CH_2Br); 7.78-7.87 (m, 2H, H_6, H_7); 8.19-8.29 (m, 2H, H_5, H_8); Anal. Calcd for $C_{12}H_6NO_3Br$: C, 49.34; H, 2.07; N, 4.80. Found: C, 49.28; H, 2.09; N, 4.68. **5**, yellow solid, mp 270 °C (ethyl acetate), ^{1}H NMR ($CDCl_3$) δ 6.68 (s, 1H, $CHBr_2$); 7.82-7.87 (m, 2H, H_6, H_7); 8.24-8.30 (m, 2H, H_5, H_8); Anal. Calcd for $C_{12}H_5NO_3Br_2$: C, 38.85; H, 1.36; N, 3.78. Found: C, 39.18; H, 1.20; N, 3.68.

A mixture of **4** (1 g, 3.42 mmol) and 0.87 g (20.5 mmol) of lithium chloride in tetrahydrofuran (150 mL) was stirred at rt during 24 h under nitrogen. The reaction mixture was extracted with chloroform and the organic layer was washed with water (6 x 300 mL), dried over anhydrous Na_2SO_4 and evaporated under vacuum. The crude residue was recrystallized from methanol affording 0.78 g (92%) of **2**.

General procedure for $S_{RN}1$ reactions

✧ Norris conditions (Entry 1, Table 2)

Under nitrogen atmosphere, an aqueous solution (2.37 mL, 3.63 mmol) of 40% tetrabutylammonium hydroxide was stirred with 2-nitropropane (320 mg, 3.63 mmol) for 1 h. A solution of **2** (300 mg, 1.21 mmol) in dichloromethane (70 mL) was added and the mixture was stirred at rt during 24 h under nitrogen and irradiation with two 60 W tungsten lamps. The organic layer was separated and the aqueous layer was extracted with dichloromethane (3 x 20 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and evaporated under vacuum. The crude residue was purified by chromatography on a silica gel column, eluting with dichloromethane to give 2-isopropylidenemethylnaphth[2,3-*d*]oxazole-4,9-dione (**8a**) (115 mg, 37%). **8a**, yellow solid, mp 236 °C (isopropanol), ^{1}H NMR ($CDCl_3$) δ 2.07 (s, 3H, CH_3); 2.38 (s, 3H, CH_3); 6.29 (br s, 1H, ethylenic H); 7.74-7.81 (m, 2H, H_6, H_7); 8.16-8.23 (m, 2H, H_5, H_8). Anal. Calcd for $C_{15}H_{11}NO_3$: C, 71.14; H, 4.38; N, 5.53. Found: C, 71.30; H, 4.21; N, 5.44.

✧ Kornblum conditions (Entries 2-4, Table 2)

To a solution of 2-nitropropane lithium salt (345 mg, 3.63 mmol) in dry DMF or DMSO (20 mL), **2** (300 mg, 1.21 mmol) was added under nitrogen and anhydrous conditions. The reaction mixture was irradiated with two 60 W tungsten lamps and stirred at rt during 15 min (Entry 2), 4 h (Entry 3) or 24 h (Entry 4). Then, it was poured into water (100 mL). The aqueous solution was extracted with chloroform (3 x 50 mL). The organic extracts were washed with water (6 x 300 mL), dried over anhydrous Na_2SO_4 and evaporated under vacuum. Chromatography on a silica gel column eluting with chloroform, gave 230 mg (75%) of **8a** for Entry 4 and only degradation products for Entries 2 and 3.

Inhibition experiments

The procedure was similar to that for Entry 4 (Kornblum conditions). Cupric chloride (Entries 5 and 6), *p*-DNB (Entries 7 and 8) and TEMPO (Entry 9) were added prior to the chloride (**2**) in the reaction mixture. The Entries 10 and 12 were performed with bubbling molecular oxygen into the reaction mixture. The reaction was performed in the dark (Entries 11 and 12) by wrapping the flask with aluminum foil. The results of these respective experiments were shown in Table 2.

Preparation of the nitroalkanes and their lithium salt

The nitroalkanes were commercially available or prepared from the secondary amines by oxidation with *m*-CPBA[20,21] in refluxed 1,2-dichloroethane for 3 h (**6b-i**) and 2,2-dimethyl-5-nitro-1,3-dioxane (**6j**) was obtained as previously described.[21]

A lithium methoxide solution was prepared by careful addition of lithium (175 mg, 0.025 at. g) to methanol (15 mL). After the solution had become clear, the nitroalkane (25 mmol) was added. The solution was stirred at rt for 2 h and concentrated under vacuum. When the solution became viscous, about 300 mL of ether was added to cause precipitation. The lithium salt was filtered, washed with ether and kept under oil-pump vacuum for 24 h.

$S_{RN}1$ reactions with the different lithium salts

All the reactions were performed with the Kornblum conditions of the Entry 4 (Table 2), using 300 mg (1.21 mmol) of the chloride (**2**) and 3 equivalents of the lithium salt. The crude residues were treated like those of the Entry 4 to give the required compounds.

2-(2-Methylpenten-1-yl)naphth[2,3-*d*]oxazole-4,9-dione (8b)

Yellow solid, 71% yield, *E*/*Z* = 4/1, mp 199 °C (isopropanol), *E* isomer: ^{1}H NMR ($CDCl_3$) δ 0.96 (t, J = 7.4 Hz, 3H, $CH_2C\underline{H}_3$); 1.60 (sextet, J = 7.4 Hz, 2H, $C\underline{H}_2CH_3$); 2.31 (t, J = 7.4 Hz, 2H, allylic CH_2); 2.39 (d, J = 0.9 Hz, 3H, CCH_3); 6.32 (d, J = 0.9 Hz, 1H, ethylenic H); 7.75-7.82 (m, 2H, H_6, H_7); 8.18-8.27 (m, 2H, H_5, H_8). *Z* isomer: ^{1}H NMR ($CDCl_3$) δ 1.02 (t, J = 7.4 Hz, 3H, $CH_2C\underline{H}_3$); 1.26 (sextet, J = 7.4 Hz, 2H, $C\underline{H}_2CH_3$); 2.07 (d, J = 1.3 Hz, 3H, CCH_3); 2.85 (t, J = 7.4 Hz, 2H, allylic CH_2); 6.32 (d, J = 1.3 Hz, 1H, ethylenic H); 7.75-7.82 (m, 2H, H_6, H_7); 8.18-8.27 (m, 2H, H_5, H_8). Anal. Calcd for $C_{17}H_{15}NO_3$: C, 72.58; H, 5.37; N, 4.98. Found: C, 72.97; H, 5.16; N, 4.83.

2-(2,5-Dimethylhexen-1-yl)naphth[2,3-*d*]oxazole-4,9-dione (8c)

Yellow solid, 74% yield, *E*/*Z* = 4/1, mp 201 °C (isopropanol), *E* isomer: ^{1}H NMR ($CDCl_3$) δ 0.89 [d, J = 6.6 Hz, 6H, $(CH_3)_2$]; 1.15-1.64 (m, 3H, $CHCH_2$); 2.30 (t, J = 7.3 Hz, 2H, allylic CH_2); 2.39 (d, J = 0.9 Hz, 3H, CCH_3); 6.32 (d, J = 0.9 Hz, 1H, ethylenic H); 7.75-7.82 (m, 2H, H_6, H_7); 8.18-8.27 (m, 2H, H_5, H_8). *Z* isomer: ^{1}H NMR ($CDCl_3$) δ 0.89 [d, J = 6.6 Hz, 6H, $(CH_3)_2$]; 1.15-1.64 (m, 3H, $CHCH_2$); 2.07 (d, J = 1.2 Hz, 3H, CCH_3); 2.86 (t, J = 7.3 Hz, 2H, allylic CH_2); 6.32 (d, J = 1.2 Hz, 1H, ethylenic H); 7.75-7.82 (m, 2H, H_6, H_7); 8.18-8.27 (m, 2H, H_5, H_8). Anal. Calcd for $C_{19}H_{19}NO_3$: C, 73.77; H, 6.19; N, 4.53. Found: C, 73.24; H, 6.34; N, 4.04.

2-Cyclopentylidenemethylnaphth[2,3-*d*]oxazole-4,9-dione (8d)

Yellow solid, 58% yield, mp 231 °C (isopropanol), ^{1}H NMR ($CDCl_3$) δ 1.71-1.95 [m, 4H, $(CH_2)_2$]; 2.63 (t, J = 6.4 Hz, 2H, allylic CH_2); 2.98 (t, J = 6.4 Hz, 2H, allylic CH_2); 6.48 (br s, 1H, ethylenic H); 7.73-7.81 (m, 2H, H_6, H_7); 8.16-8.26 (m, 2H, H_5, H_8). Anal. Calcd for $C_{17}H_{13}NO_3$: C, 73.11; H, 4.69; N, 5.01. Found: C, 72.88; H, 4.57; N, 4.92.

2-Cyclohexylidenemethylnaphth[2,3-*d*]oxazole-4,9-dione (8e)

Yellow solid, 66% yield, mp 223 °C (isopropanol), ^{1}H NMR ($CDCl_3$) δ 1.51-1.88 [m, 6H, $(CH_2)_3$]; 2.38 (t, J = 5.4 Hz, 2H, allylic CH_2); 3.05 (t, J = 5.4 Hz, 2H, allylic CH_2); 6.24 (br s, 1H, ethylenic H); 7.73-7.81 (m, 2H, H_6, H_7); 8.16-8.27 (m, 2H, H_5, H_8). Anal. Calcd for $C_{18}H_{15}NO_3$: C, 73.71; H, 5.15; N, 4.78. Found: C, 73.14; H, 5.00; N, 4.72.

2-Cycloheptylidenemethylnaphth[2,3-*d*]oxazole-4,9-dione (8f)

Yellow solid, 71% yield, mp 249 °C (isopropanol), ^{1}H NMR ($CDCl_3$) δ 1.59-1.83 [m, 8H, $(CH_2)_4$]; 2.56 (t, J = 5.4 Hz, 2H, allylic CH_2); 3.10 (t, J = 5.4 Hz, 2H, allylic CH_2); 6.34 (br s, 1H, ethylenic H); 7.73-7.82 (m, 2H, H_6, H_7); 8.18-8.27 (m, 2H, H_5, H_8). Anal. Calcd for $C_{19}H_{17}NO_3$: C, 74.25; H, 5.58; N, 4.56. Found: C, 74.28; H, 5.33; N, 4.44.

2-Cyclododecylidenemethylnaphth[2,3-*d*]oxazole-4,9-dione (8g)

Yellow solid, 65% yield, mp 237 °C (ethyl acetate), ^{1}H NMR ($CDCl_3$) δ 1.32-1.37 [m, 14H, $(CH_2)_7$]; 1.67-1.70 [m, 4H, $(CH_2)_2$]; 2.40 (t, J = 6.6 Hz, 2H, allylic CH_2); 2.98 (t, J = 6.6 Hz, 2H, allylic CH_2); 6.42 (br s, 1H, ethylenic H); 7.76-7.82 (m, 2H, H_6, H_7); 8.18-8.27 (m, 2H, H_5, H_8). Anal. Calcd for $C_{24}H_{27}NO_3$: C, 76.36; H, 7.21; N, 3.71. Found: C, 76.44; H, 7.32; N, 3.55.

2-(1,2,3,4-Tetrahydronaphthalen-1-ylidenemethyl)naphth[2,3-*d*]oxazole-4,9-dione (8h)

Orange solid, 70% yield, *E* isomer, mp 270 °C (isopropanol), ^{1}H NMR ($CDCl_3$) δ 1.96 (quintet, J = 6.1 Hz, 2H, CH_2-C<u>H$_2$</u>-CH_2); 2.86 (t, J = 6.1 Hz, 2H, benzylic CH_2); 3.41 (t, J = 6.1 Hz, 2H, allylic CH_2); 7.03 (br s, 1H, ethylenic H); 7.19-7.37 (m, 3H, benzenic H); 7.73-7.84 (m, 3H, H_6, H_7, benzenic H); 8.21-8.30 (m, 2H, H_5, H_8). Anal. Calcd for $C_{22}H_{15}NO_3$: C, 77.41; H, 4.43; N, 4.10. Found: C, 77.55; H, 4.31; N, 3.83.

2-(2-Phenylpropen-1-yl)naphth[2,3-*d*]oxazole-4,9-dione (8i)

Yellow solid, 58% yield, *E*/*Z* = 4/1, mp 249 °C (isopropanol), *E* isomer: ^{1}H NMR ($CDCl_3$) δ 2.84 (d, J = 1.2 Hz, 3H, CH_3); 6.84 (d, J = 1.2 Hz, 1H, ethylenic H); 7.42-7.47 (m, 3H, benzenic H); 7.57-7.62 (m, 2H, benzenic H); 7.76-7.85 (m, 2H, H_6, H_7); 8.21-8.30 (m, 2H, H_5, H_8). *Z* isomer: ^{1}H NMR ($CDCl_3$) δ 2.38 (d, J = 1.4 Hz, 3H, CH_3); 6.62 (d, J = 1.4 Hz, 1H, ethylenic H); 7.42-7.47 (m, 3H, benzenic H); 7.57-7.62 (m, 2H, benzenic H); 7.76-7.85 (m, 2H, H_6, H_7); 8.21-8.30 (m, 2H, H_5, H_8). Anal. Calcd for $C_{20}H_{13}NO_3$: C, 76.18; H, 4.16; N, 4.44. Found: C, 76.43; H, 4.02; N, 4.30.

2-(2,2-Dimethyl-1,3-dioxan-5-ylidenemethyl)naphth[2,3-*d*]oxazole-4,9-dione (8j)

Yellow solid, 60% yield, mp 203 °C (isopropanol), ^{1}H NMR ($CDCl_3$) δ 1.45 [s, 6H, $(CH_3)_2$]; 4.44 (br s, 2H, CH_2O); 5.05 (br s, 2H, CH_2O); 6.28 (br s, 1H, ethylenic H); 7.78-7.82 (m, 2H, H_6, H_7); 8.20-8.27 (m, 2H, H_5, H_8). Anal. Calcd for $C_{18}H_{15}NO_5$: C, 66.46; H, 4.65; N, 4.31. Found: C, 66.32; H, 4.38; N, 4.35.

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