Synthetic Exploitation of the Ring-Opening of 3,4-Dinitrothiophene. Part 4 [1]. Synthesis of 1,4-Disubstituted 3-Hydroximino-2-nitro-1-butenes and their Cyclization to 4-Nitroisoxazoles

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The reduction of a single nitrovinyl moiety in 1,4-dialkyl- and 1,4-diaryl-2,3-dinitro-1,3-butadienes **1** with stannous chloride dihydrate in ethyl acetate furnishes the corresponding 3-hydroximino-2-nitro-1-butenes **4** in satisfactory yields. The oxidative cyclization of the latter compounds gives variable yields of 3,5-disubstituted 4-nitroisoxazoles **5**, most likely arising from aromatization of the corresponding 4,5-dihydroisoxazoles, formed through an intramolecular Michael addition of the hydroximino group in **4** to the nitroalkene functionality. In the case of the 1-naphthyl derivative **4d** such oxidative cyclization mainly leads to the competitive formation of 3-[(1-naphthyl)methyl]-2-nitrobenzo[*f*]quinoline *N*-oxide **7**.

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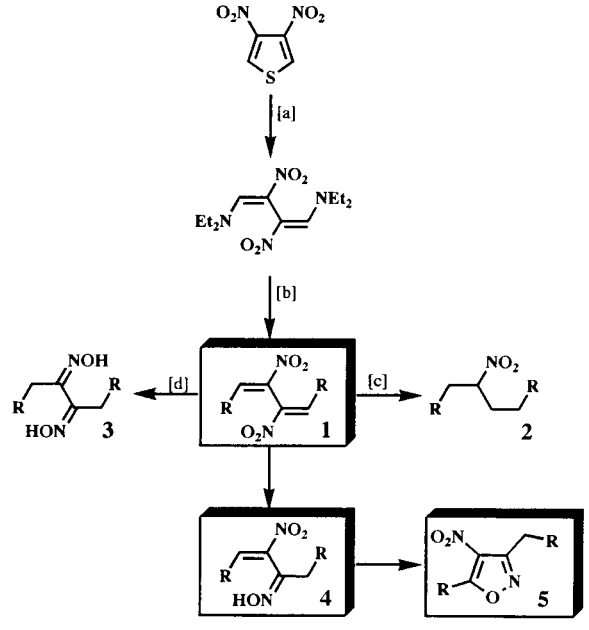
Introduction.

In previous papers [1,2] we have shown (Scheme 1) that the ring-opening reaction of 3,4-dinitrothiophene with diethylamine and the subsequent treatment of the ensuing 1,4-bis(diethylamino)-2,3-dinitro-1,3-butadiene with organomagnesium or organolithium reagents furnishes previously unknown 1,4-dialkyl- and 1,4-diaryl-2,3-dinitro-1,3-butadienes **1**. Compounds **1** are interesting synthetic segments indeed, amenable to further transformations, which should associate the intriguing properties of both electron-deficient dienes [3-5] and of 1-nitroalkenes [6-8].

The reductions [1,2a] of dinitrobutadienes **1** to either 1,4-disubstituted 2-nitrobutanes **2** or 2,3-butanedione dioximes **3** provided incentive for developing a more selective reduction method for the transformation of **1** into the corresponding nitrovinyloximes **4** (Scheme 1). We report herein on the successful outcome of this search as well as on the utilization of compounds **4** for the synthesis of substituted isoxazoles **5**.

Scheme 1



[a] Diethylamine/Ethanol, 0 °C; [b] RMgBr/THF, 0 °C; [c] Polymer supported borohydride/Methanol, 25 °C; [d] Lead powder/DMF-AcOH, 25 °C.

Results and Discussion.

Synthesis of Substituted 3-Hydroximino-2-nitro-1-butenes.

Our study was initially focussed on the development of a convenient method for the selective reduction of a single nitrovinyl functionality in the model substrate 1,4-diphenyl-2,3-dinitro-1,3-butadiene **1a**. Various conditions and reducing agents (capable to transform 1-nitroalkenes into the corresponding oximes) [6-9] were tried and, among them, the treatment of **1a** with tin(II) chloride dihydrate [9] proved to be the overall most convenient procedure. Thus, with two molar equivalents of such reductant in ethyl acetate (3 hours, room temperature) **1a** furnished, besides 26% of unreacted starting material, 55% of 1,4-diphenyl-3-hydroximino-2-nitro-1-butene (**4a**) and 6% of 1,4-diphenyl-2,3-bis(hydroximino)butane (**3a**). Longer reaction times did not result in a further, substantial, reduction of **1a** but rather caused decrease in the yield of **4a** accompanied by the formation of tarry materials. Taking into account that the transformations **1a** → **4a** and **1a** → **3a** respectively require two and four moles of tin(II) per mole of **1a**, it is intriguing that the reaction becomes very sluggish (tlc) after the consumption of *ca.* 70% of reductant. Such marked decrease in the reaction rate could possibly be related to some complexation of tin(II) by oximes **4a** and **3a** which lowers its reducing power. As a matter of

fact, the use of four moles of tin(II) chloride per mole of **1a** does cause the complete disappearance of the starting dinitrobutadiene, but with only a 50% conversion to the dioxime **3a** while 41% of the partially reduced "precursor" **4a** still remains unreacted. As expected, control experiments show that isolated **4a** undergoes reduction to **3a** by stannous chloride in ethyl acetate; such reaction however appears extremely sluggish when compared with the smooth and efficient transformation of the same compound into **3a** under the conditions (lead powder in DMF/acetic acid) previously [2a] used for the direct synthesis of **3a** from **1a**. It is interesting to note that, in the reductions of dinitrobutadienes **1** under the latter conditions [2a], 3-hydroximino-2-nitro-1-butene precursors of 2,3-bis(hydroximino)butanes could never be detected even at lower temperature and at short reaction times.

The reducing system based on the use of two molar equivalents of tin(II) chloride appeared therefore sufficiently selective and exploitable for a convenient general preparation of 1,4-disubstituted 3-hydroximino-2-nitro-1-butenes **4** and the results from the reactions of some dinitrobutadienes **1** are accordingly given in Table 1.

Table 1

Reduction of Dinitrobutadienes **1a-h** with Tin(II) Chloride Dihydrate in Ethyl Acetate [a]

Substrate	R	Recovered **1** (%) [b]	Yield (%) [b] **4a-g** [c]	**3a-g**
1a	phenyl	26	55 (74)	6
1b	2-MeC_6H_4	24	59 (78)	8
1c	4-MeC_6H_4	28	54 (75)	9
1d	1-naphthyl	17	58 (70)	7
1e	2-thienyl	47	14 (26)	trace
1f	Et	35	25 (38)	15
1g	c-C_6H_{11}	35	37 (57)	5
1h	4-$MeOC_6H_4$	97	-	-

[a] Conditions: [**1**] = 0.1 *M*, [tin(II) chloride dihydrate] = 0.2 *M*; room temperature, 3 hours. [b] Yields of products isolated by chromatography; for compounds **4a-g** yields in parentheses are calculated on the basis of the reacted substrate; [c] An (*E,E*) configuration has been tentatively attributed to compounds **4a-g** on the basis of the ^1H nmr spectra (see Experimental).

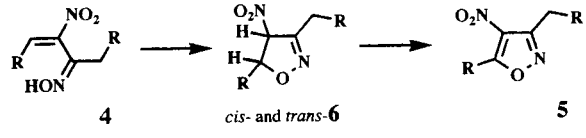
The following observations can be made on the obtained results: a) Diaryl-substituted dinitrobutadienes **1a-d** give satisfactory yields of the corresponding **4** with a good overall balance. b) The reduction of the 2-thienyl derivative **1e** is much less efficient, giving a poor yield of **4e** together with some by-products, which were not investigated, and tarry material. c) In the case of the *p*-anisyl derivative **1h**, the envisageable through-conjugation between the *p*-methoxy substituents and the nitro groups brings about a less easy reducibility of the nitrovinyl moieties so that the substrate is quantitatively recovered even after prolonged reaction times. This confirms, in the reactions studied, the involvement of a relatively mild reducing agent, possessing a higher degree of selectivity than the previously [2a] employed lead in DMF/acetic acid, which effectively reduces **1h** to the corresponding dioxime **3h**. d) With respect to the diaryl-substituted substrates **1a-d**, the reduction of the dialkyl analogues **1f** and **1g** shows, although the material balance is satisfactory, a lower selectivity with a decreased yield of the desired transformation into **4f** and **4g**.

It is worth stressing that in all the cases examined the unreacted substrates **1** can be easily recovered by chromatography and recycled. In conclusion, though the development of more efficient reducing systems with a still higher degree of selectivity seems to be desirable, the stannous chloride reduction of 1,4-diaryl- and 1,4-dialkyl-2,3-dinitro-1,3-butadienes **1** appears to be an interesting approach to hitherto unknown 3-hydroximino-2-nitro-1-butenes whose utility in organic synthesis has to be explored.

Synthesis of 3,5-Disubstituted 4-Nitroisoxazoles.

The facile intramolecular oxidative cyclizations of α,β-unsaturated oximes [10-18] together with the presence in **4a** of a nitrovinyl moiety, whose remarkable propensity to Michael additions is well known [6,19], suggested the possibility of an easy intramolecular addition yielding **6a** (Scheme 2). Actually, when **4a** was adsorbed on a silica gel preparative thin layer and left four days in the dark, elution with dichloromethane and successive workup gave (besides recovered substrate and some tarry material): i) a mixture of the two diastereomeric 4,5-dihydroisoxazoles **6a** which, because of the too small quantity obtained, could be identified only on the grounds of their ^1H nmr absorptions [20]; ii) a product which was identified, on the basis of elemental analysis and ^1H nmr data, as 3-benzyl-4-nitro-5-phenylisoxazole **5a**.

Scheme 2



4 *cis*- and *trans*-**6** **5**

a : R = Ph

The above findings and the interest of isoxazoles as target molecules [21] prompted us to investigate the behavior of **4a** under some conditions previously utilized for intramolecular oxidative cyclizations of α,β-unsaturated oximes or for aromatization of 4,5-dihydroisoxazoles. As shown in experiments 1-3 of Table 2, isoxazole **5a** was obtained when **4a** was refluxed either in dioxane with DDQ (method A) [22], in aqueous tetrahydrofuran with iodine/potassium iodide and sodium bicarbonate

Table 2

Cyclization Reactions of 3-Hydroximino-2-nitro-1-butenes **4a-g** to the Corresponding Isoxazoles **5a-g**

Experiment	R	Method [a], time (hours) [b]	Product	Yield (%) [c]
1	phenyl	A, 2.5	**5a**	61
2		B, 2.0		50
3		C, 4.5		40
4	2-MeC_6H_4	A, 2.0	**5b**	57
5	4-MeC_6H_4	A, 1.5	**5c**	50
6	1-naphthyl	A, 1.7	**5d**	5 [d]
7		B, 3.0		30 [e]
8	2-thienyl	A, 2.5	**5e**	7
9		B, 2.0		20
10	Et	A, 3.0	**5f**	12
11		B, 1.5		20
12	c-C_6H_{11}	A, 24.0	**5g**	15 [f]
13		B, 1.7		48

[a] Reactions performed at reflux temperature; A: dioxane/DDQ, B: THF/aqueous sodium bicarbonate/aqueous iodine-potassium iodide, C: dioxane/manganese dioxide. [b] As determined by tlc disappearance of **4**. [c] Yields of products isolated by chromatography. [d],[e] Benzoquinoline *N*-oxide **7** also isolated ([d]: 26%, [e]: 47%). [f] Unreacted **4g** (51%) recovered.

(method B) [10], or in dioxane with active γ-manganese dioxide (method C) [23]: the best yields in isoxazole **5a** being observed with method A.

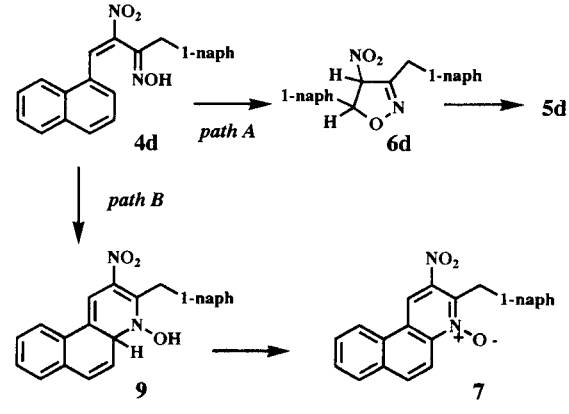
The extension of the latter procedure to the 3-hydroximino-2-nitro-1-butenes **4b-g** (Table 2) showed comparable results only for the benzene analogues **4b** and **4c**. For substrates **4d-g**, on the other hand, method B appeared preferable as improved yields of **5d-g** (though somehow satisfactory only for **5g**) were obtained in shorter reaction times. The low yields of the dialkyl-substituted isoxazole **5f** can be related to an unefficient oxidation of its 4,5-dihydroisoxazole precursors. The formation of significant quantities of degradation products during oxidative aromatization of alkyl-substituted 4,5-dihydroisoxazoles is not unprecedented [17,24,25]. Similar oxidative demolitions were also observed in experiments 8 and 9 carried out with the 2-thienyl derivative **4e**.

The 1-naphthyl derivative **4d** shows an interesting behavior which is remarkably different from that of the benzene derivatives **4a-c**. Actually, besides **5d**, the oxidative cyclization of **4d** furnishes (Scheme 3) 3-[(1-naphthyl)-methyl]-2-nitrobenzo[*f*]quinoline *N*-oxide **7** as the main reaction product, the use of method B resulting in a substantial increase in the yields of both products. The structure of **7** was assigned on the basis of its elemental analysis and ^1H nmr spectrum which includes in particular a singlet (δ 9.53) and an AB system (δ 8.44 and 8.59) respectively attributable to H(1) and H(5)-H(6) of the benzo[*f*]quinoline *N*-oxide ring. Further evidence for structure **7** was obtained from its *N*-deoxygenation reaction [26] with phosphorus trichloride in chloroform to give the corresponding benzoquinoline **8**.

To explain the formation of products **5d** and **7** from **4d** a competition between two oxidative cyclization paths (A and B of Scheme 3) can be envisaged. Path A involves attack of the hydroximino oxygen on the nitrovinyl moiety of **4d** with formation of the 4,5-dihydroisoxazole **6d**, precursor of **5d**. In the competitive path B, on the other hand, the hydroximino nitrogen would attack the naphthalene C(2), a vinylogous position activated by the conjugation with the side-chain nitro group, the so-formed intermediate **9** then aromatizing under the oxidative reaction conditions. It is interesting to note that such competition was not observed in the case of **4a**, the benzene analogue of **4d**. Such an outcome can be rationalized when considering that in the case of the naphthalene substrate the formation of the 4,5-dihydroisoxazole **6d** is not sterically favored. Furthermore, a fundamental role in favoring the formation of **9** (and hence path B) may be played by the higher double-bond localization in the naphthalene moiety when compared with a benzene ring.

In conclusion, the reduction of 1,4-dialkyl- and 1,4-diaryl-2,3-dinitro-1,3-butadienes to the corresponding 3-hydroximino-2-nitro-1-butenes and the oxidative cyclization of the latter can be considered with some noted limitations, a route to 3,5-disubstituted 4-nitroisoxazoles alternative to other methods suffering from moderate yields [27] and/or involving intermediates not easily available [27,28]. The cyclization of the naphthalene derivative **4d** to **7**, in our opinion, represents an example of access to the benzo[*f*]quinoline ring that is worthy of further investigation.

Scheme 3



EXPERIMENTAL

Melting points were determined on a Büchi 535 apparatus and are uncorrected. The ^1H nmr spectra were taken on a Varian Gemini 200 spectrometer. TMS was used as the internal standard and chemical shifts are reported as δ values (ppm).

Petroleum ether and light petroleum refer to the fractions with bp 40-60° and 80-100°, respectively. Dinitrobutadienes **1a-h** were synthesized as reported [2a]. Dioximes **3a-g** were identified

by comparison (tlc, ^{1}H nmr) with authentic samples from our laboratory [2a].

General Procedure for the Reduction of Dinitrobutadienes **1a-h** with Tin(II) Chloride Dihydrate.

In an Erlenmeyer flask, dinitrobutadiene **1** (1.7 mmoles) was dissolved in 17 ml of ethyl acetate. Under magnetic stirring, tin(II) chloride dihydrate (0.76 g, 3.4 mmoles) was added and the reaction solution was allowed to stand 3 hours at room temperature. The reaction mixture was then poured into ice-water and the *p*H adjusted to *ca.* 7 with 5% aqueous sodium bicarbonate. The usual workup involved six extractions with ether, drying of the ether extracts with sodium sulfate, distillation of the solvent in a rotary-evaporator and column chromatography of the residue on silica gel (eluants: dichloromethane or petroleum ether-diethyl ether gradients).

As far as the stereochemistry of the isolated **4a-g** is regarded, an (*E,E*) configuration can be confidently attributed on the grounds [2a] of the chemical shift values both of the vinyl protons (*cis* to the nitro group) and of the NOH protons in DMSO-d_6 (δ NOH) as compared with the corresponding values [2a] of the relevant dinitrobutadienes **1** and dioximes **3**.

1,4-Diphenyl-3-hydroximino-2-nitro-1-butene (**4a**).

The compound was crystallized from light petroleum, mp 93.0-95.0°; ^{1}H nmr (acetone-d_6): δ 4.03 (2H, s), 7.40 (10H, m), 8.08 (1H, s) and 11.33 (1H, s); δ NOH (DMSO): 12.17.

Anal. Calcd. for $C_{16}H_{14}N_2O_3$: C, 68.07; H, 5.00; N, 9.92. Found: C, 67.95; H, 4.95; N, 9.78.

1,4-Bis(2-methylphenyl)-3-hydroximino-2-nitro-1-butene (**4b**).

This compound was crystallized from light petroleum, mp 126.9-127.6°; ^{1}H nmr (deuteriochloroform): δ 1.91 (3H, s), 2.02 (3H, s), 3.95 (2H, s), 6.97 (6H, m), 7.30 (2H, m), 8.11 (1H, br s) and 8.20 (1H, s); δ NOH (DMSO): 12.24.

Anal. Calcd. for $C_{18}H_{18}N_2O_3$: C, 69.66; H, 5.84; N, 9.03. Found: C, 69.70; H, 6.02; N, 9.10.

1,4-Bis(4-methylphenyl)-3-hydroximino-2-nitro-1-butene (**4c**).

This compound was crystallized from light petroleum, mp 143.8-144.5°; ^{1}H nmr (acetone-d_6): δ 2.19 (3H, s), 2.36 (3H, s), 3.98 (2H, s), 6.96 (4H, AA'BB', J = 8.1 Hz), 7.19 and 7.41 (2H each, AA'BB', J = 8.2 Hz), 8.03 (1H, s) and 11.23 (1H, s); δ NOH (DMSO): 12.10.

Anal. Calcd. for $C_{18}H_{18}N_2O_3$: C, 69.66; H, 5.84; N, 9.03. Found: C, 69.82; H, 5.89; N, 9.11.

1,4-Bis(1-naphthyl)-3-hydroximino-2-nitro-1-butene (**4d**).

This compound was crystallized from light petroleum, mp 151.7-153.8°; ^{1}H nmr (acetone-d_6): δ 4.39 (2H, s), 7.08 (5H, m), 7.37 (6H, m), 7.75 (3H, m), 8.55 (1H, s) and 11.60 (1H, s); δ NOH (DMSO): 12.44.

Anal. Calcd. for $C_{24}H_{18}N_2O_3$: C, 75.38; H, 4.74; N, 7.32. Found: C, 75.12; H, 4.81; N, 7.26.

1,4-Bis(2-thienyl)-3-hydroximino-2-nitro-1-butene (**4e**).

This compound was an oil which darkened on standing; ^{1}H nmr (deuteriochloroform): δ 4.29 (2H, s), 6.79 (2H, m), 7.17 (2H, m), 7.69 (1H, d of m, J = 3.1 Hz), 7.85 (1H, dd, J = 1.2 and 5.3 Hz), 8.37 (1H, s) and 11.35 (1H, s). As no analytically pure sample could be obtained, the product was reduced with lead powder in DMF-acetic acid and characterized as 1,4-bis(2-thienyl)-2,3-bis(hydroximino)butane [2a].

6-Hydroximino-5-nitro-4-octene (**4f**).

This product was obtained as an oil; ^{1}H nmr (acetone-d_6): δ 0.94 (3H, t, J = 7.2 Hz), 1.11 (3H, t, J = 7.5 Hz), 1.47 (2H, m), 2.32 (2H, quint, J = 7.5 Hz), 2.53 (2H, m), 7.32 (1H, t, J = 7.5 Hz) and 10.82 (1H, s); δ NOH (DMSO): 14.7.

Anal. Calcd. for $C_8H_{14}N_2O_3$: C, 51.60; H, 7.58; N, 15.04. Found: C, 51.80; H, 7.69; N, 15.21.

The product was also characterized as 4,5-bis(hydroximino)octane [2a] *via* lead reduction in DMF-acetic acid.

1,4-Dicyclohexyl-3-hydroximino-2-nitro-1-butene (**4g**).

This product was crystallized from light petroleum, mp 127.5-128.2°; ^{1}H nmr (deuteriochloroform): δ 1.24 (10H, m), 1.69 (11H, m), 2.34 (1H, m), 2.50 (2H, d, J = 7.0 Hz), 7.15 (1H, d, J = 11.4 Hz) and 8.24 (1H, br s); δ NOH (DMSO): 11.75.

Anal. Calcd. for $C_{16}H_{26}N_2O_3$: C, 65.28; H, 8.90; N, 9.51. Found: C, 65.13; H, 9.15; N, 9.26.

General Procedures for the Oxidative Cyclization of Compounds **4a-g**.

The oxidative cyclization of 3-hydroximino-2-nitro-1-butenes **4a-g** was carried out using either of the three methods reported below. Reaction times and yields are collected in Table 2. Method C was only tried for the phenyl derivative **4a**. Method A involves refluxing of a 0.03 molar solution of **4** in dry dioxane with three molar equivalents of DDQ [22]. In method B compound **4** (0.35 mmole) was treated with iodine-potassium iodide (0.09 g and 0.2 g respectively in 0.8 ml of water) in refluxing aqueous bicarbonate (0.12 g in 1.1 ml of water) and tetrahydrofuran (1.3 ml) [10]. In method C compound **4** (0.02 molar in dioxane) was refluxed [23] in the presence of 16 molar equivalents of freshly prepared [29] γ-manganese dioxide. After the refluxing time reported in Table 2, the reaction solutions were cooled and poured into brine. The usual workup involved extraction with ether, drying of the extracts over sodium sulfate and evaporation of the solvent in a rotary evaporator. The residue was then chromatographed on a silica gel column eluting with gradients of petroleum ether-dichloromethane.

3-Benzyl-4-nitro-5-phenylisoxazole (**5a**).

This product was crystallized from light petroleum, mp 75.5-76.9°; ^{1}H nmr (deuteriochloroform): δ 4.37 (2H, s), 7.33 (5H, m), 7.55 (3H, m) and 7.89 (2H, m).

Anal. Calcd. for $C_{16}H_{12}N_2O_3$: C, 68.56; H, 4.31; N, 9.99. Found: C, 68.51; H, 4.28; N, 10.00.

5-(2-Methylphenyl)-3-[(2-methylphenyl)methyl]-4-nitroisoxazole (**5b**).

This compound was crystallized from light petroleum, mp 82.4-82.8°; ^{1}H nmr (deuteriochloroform): δ 2.27 (3H, s), 2.43 (3H, s), 4.39 (2H, s), 7.20 (4H, m) and 7.40 (4H, m).

Anal. Calcd. for $C_{18}H_{16}N_2O_3$: C, 70.12; H, 5.23; N, 9.08. Found: C, 70.20; H, 5.12; N, 8.96.

5-(4-Methylphenyl)-3-[(4-methylphenyl)methyl]-4-nitroisoxazole (**5c**).

This compound was crystallized from light petroleum, mp 98.0-98.8°; ^{1}H nmr (deuteriochloroform): δ 2.32 (3H, s), 2.44 (3H, s), 4.32 (2H, s), 7.13 and 7.25 (2H each, AA'BB', J = 8.2 Hz), 7.33

and 7.78 (2H each, AA'BB', J = 8.1 Hz).

Anal. Calcd. for $C_{18}H_{16}N_2O_3$: C, 70.12; H, 5.23; N, 9.08. Found: C, 70.03; H, 5.12; N, 9.00.

5-(1-Naphthyl)-3-[(1-naphthyl)methyl]-4-nitroisoxazole (**5d**).

This compound was crystallized from light petroleum/toluene, mp 112.1-114.5°; ^{1}H nmr (deuteriochloroform): δ 4.92 (2H, s), 7.55 (9H, m), 7.83 and 7.89 [3H in all, partly overlapped m and d (J = 8.4 Hz)], 8.05 (1H, d, J = 8.1 Hz) and 8.25 (1H, d, J = 8.2 Hz).

Anal. Calcd. for $C_{24}H_{16}N_2O_3$: C, 75.78; H, 4.24; N, 7.36. Found: C, 75.96; H, 4.20; N, 7.16.

4-Nitro-5-(2-thienyl)-3-[(2-thienyl)methyl]isoxazole (**5e**).

This product was purified by sublimation (80°/0.05 mm Hg), mp 116.5-118.0°; ^{1}H nmr (deuteriochloroform): δ 4.59 (2H, s), 6.94 (1H, dd, J = 3.4 and 5.1 Hz), 7.01 (1H, dd, J = 3.4 and 1.1 Hz), 7.21 (1H, dd, J = 1.1 and 5.1 Hz), 7.29 (1H, dd, J = 4.0 and 5.0 Hz), 7.83 (1H, dd, J = 1.2 and 5.0 Hz) and 8.25 (1H, dd, J = 1.2 and 4.0 Hz).

Anal. Calcd. for $C_{12}H_8N_2O_3S_2$: C, 49.30; H, 2.76; N, 9.58. Found: C, 49.61; H, 2.91; N, 9.43.

5-Ethyl-4-nitro-3-propylisoxazole (**5f**).

This product was obtained as an oil; ^{1}H nmr (deuteriochloroform): δ 1.03 (3H, t, J = 7.5 Hz), 1.39 (3H, t, J = 7.6 Hz), 1.76 (2H, sext, J = 7.5 Hz), 2.94 (2H, t, J = 7.5 Hz) and 3.23 (2H, t, J = 7.6 Hz).

Anal. Calcd. for $C_8H_{12}N_2O_3$: C, 52.17; H, 6.57; N, 15.21. Found: C, 52.29; H, 6.81; N, 15.40.

5-Cyclohexyl-3-[(cyclohexyl)methyl]-4-nitroisoxazole (**5g**).

This product was purified by sublimation (100°/0.05 mm Hg), mp 51.0-53.3°; ^{1}H nmr (deuteriochloroform): δ 1.21 and 1.69 (21H in all, two partly overlapped multiplets), 2.83 (2H, d, J = 6.6 Hz) and 3.55 (1H, tt, J = 3.4 and 11.4 Hz).

Anal. Calcd. for $C_{16}H_{24}N_2O_3$: C, 65.73; H, 8.27; N, 9.58. Found: C, 65.85; H, 8.43; N, 9.60.

3-[(1-Naphthyl)methyl]-2-nitrobenzo[*f*]quinoline *N*-Oxide (**7**).

This product was crystallized from toluene, mp 209.3-210.0°; ^{1}H nmr (DMSO-d_6): δ 5.07 (2H, s), 6.86 (1H, d, J = 7.1 Hz), 7.30 (1H, app. t, J = 8.2 Hz), 7.61 (2H, m), 7.80 and 7.92 [4H in all, d (J = 8.4 Hz) partly overlapped with a multiplet], 8.24 (2H, m), 8.44 and 8.59 (1H each, AB, J = 9.4 Hz), 9.08 (1H, m) and 9.53 (1H, s).

Anal. Calcd. for $C_{24}H_{16}N_2O_3$: C, 75.78; H, 4.24; N, 7.36. Found: C, 76.02; H, 4.35; N, 7.41.

3-[(1-Naphthyl)methyl]-2-nitrobenzo[*f*]quinoline (**8**).

This compound was obtained in 67% yield by reduction of **7** with phosphorus trichloride in chloroform [26] and crystallized from light petroleum-toluene, mp 182.0-182.6°; ^{1}H nmr (acetone-d_6): δ 5.22 (2H, s), 7.16 (1H, d, J = 7.0 Hz), 7.38 (1H, app. t, J = 8.2 Hz), 7.52 (2H, m), 7.87 (5H, m), 8.14 (1H, m), 8.30 (2H, app. d, J = 8.7 Hz), 8.95 (1H, m) and 9.77 (1H, s).

Anal. Calcd. for $C_{24}H_{16}N_2O_2$: C, 79.10; H, 4.42; N, 7.69. Found: C, 79.32; H, 4.40; N, 7.86.

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