Convenient Preparation of 1,2-Alkylenedioxybenzofuroxans and Benzofurazans

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Nitration of the dioxolo-annelated benzenes **11** led to the corresponding dinitro derivatives **12**. Nucleophilic substitution of the latter with azide ion furnished the monoazides **13** which on thermolysis afforded the benzofuroxans **14**. Deoxygenation of furoxans **1a,b,e,f, 2a-c,e,f, 5, 7, 9** and **14** with triphenylphosphine, furnished the respective benzofurazans **3a,b,e,f, 4a-c,e,f, 6, 8, 10** and **15**.

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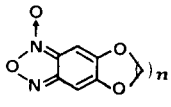
During the course of our studies on 1,2-alkylenedioxyannelated benzofuroxans and benzofurazans [1], we have reported on the preparation of the dioxolo **2a** [2a]; dioxino **1b** [2b], **2b** [2a]; dioxepino **1c**, **3c** [2c], **2c** [2a]; dioxocino **1d**, **2d**, **3d**, **4d** [2d]; dioxonino **1e**, **2e** [2a]; and dioxecino **1f**, **2f** [2a] benzofuroxans and benzofurazans. Synthesis of the five-membered furoxan **1a** [3], the acyclic **5** [3], and the furazan **6** [4] has also been published.



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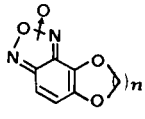

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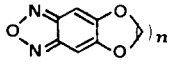

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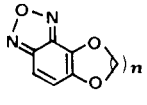

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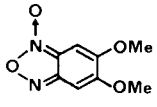

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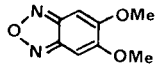

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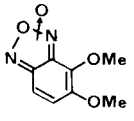

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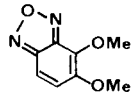

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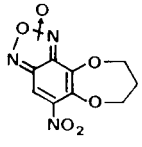
	n
a	1
b	2
c	3
d	4
e	5
f	6



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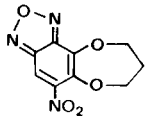

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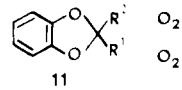
In order to complete the series, we now report preparation of the remainder of the unsubstituted benzofuroxans and benzofurazans from five- to the ten-membered heterocycles as well as the nitro-substituted dioxepino derivatives and, in addition, the "angular" benzofurazan of veratrole.

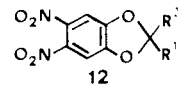
The availability of several benzofuroxan precursors [2,3], prompted us to prepare the corresponding benzofurazans by deoxygenation with excess triphenylphosphine in refluxing toluene (0.5-1.5 hours) [1-3]. Thus benzofuroxans **1a,b,e,f, 2a-c,e,f, 5, 7** and **9** furnished the corresponding benzofurazans **3a,b,e,f, 4a-c,e,f, 6, 8** and **10**, respectively. These compounds are interesting because they exhibit biological activity and, moreover, they have found many industrial applications [1].

The uv spectra of the "linear" derivatives **3a,b,e,f** are distinctly different from those of their "angular" isomers **4a-c,e,f**. The former absorb at λ max (ε) = 289-303 (8000-11000) nm, whilst the latter are bathochromically shifted, comparatively, with lower molar absorptivity, *i.e.*, λ max (ε) = 345-393 (2000-3500) nm. The ir spectra are characteristic of furazans [1], whereas in the ^{1}H nmr spectra, the pseudoaromatic protons absorb in a narrow range at δ 6.89-7.52 and are slightly deshielded relative to the corresponding furoxans [2a].

Benzo[1,3]dioxole compounds are of importance in biochemistry and in natural products synthesis [5c]. It was therefore considered that fusion of these with the furoxan or the furazan ring systems would furnish some derivatives with interesting pharmacological activity. Nitration of the known 1,2-alkylenedioxybenzenes **11** [5] with excess fum-



11



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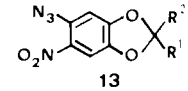

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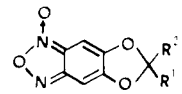
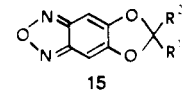


14

	R^1	R^2
a	Me	Me
b	Et	Et
c	$-(CH_2)_4-$	
d	$-(CH_2)_5-$	
e	$-(CH_2)_6-$	
f	Adamantyl	



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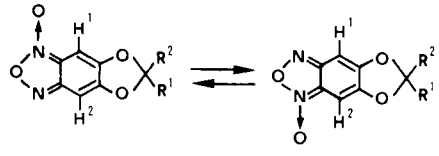
ing nitric acid (d = 1.52) was carried out in glacial acetic acid at 0-10° (0.5 hour) to give the 5,6-dinitro products **12**. Treatment of the latter with excess azide ion in dimethyl sulfoxide at ambient (2-3.5 hours), isolation of the monoazides **13** and subsequent thermolysis in refluxing benzene or toluene (2-3 hours), afforded the corresponding dioxolo-annelated benzofuroxans **14**. Deoxygenation of the latter with triphenylphosphine as described above, led to furazans **15** [1-3].

The uv spectra of furoxans **14** show absorptions at λ max (ε) = 368-374 (7000-10500) nm, while those of furazans **15** at λ max (ε) = 296-300 (13500-18000) nm which is nearly the same wavelength as that of the related "linear" furazans **3a,b,e,f** discussed above; their molar absorptivity, however, is slightly increased as a result of coplanarity of the rigid dioxole ring with the benzene nucleus thus enhancing n-π conjugation [2a,6]. The ir spectra are diagnostic of furoxans and furazans, while in the ^{1}H nmr spectra, the pseudoaromatic absorptions of the latter (δ 6.79-6.84) are somewhat deshielded compared to those of the former (δ 6.39-6.60). Noteworthy is the ^{1}H nmr separation of the two pseudoaromatic protons H^1 and H^2 at ambient in the furoxans **14**, unlike in the case of furoxans **1** [2a]. Apparently, the well known tautomeric equilibrium [1] shown below is slow enough on the nmr time-scale so that H^1 and H^2 appear as two broad singlets ($\Delta\delta$ = 0.17 ±0.02) that collapse into a singlet upon heating the tube at *ca.* 40-50°.



In conclusion, the above discussed routes: 1,2-alkylenedioxybenzene → *ortho*-dinitro derivative → *ortho*-nitro azide → furoxan → furazan are most convenient for the preparation of benzofuroxans and benzofurazans, in general.

EXPERIMENTAL

The general experimental has been described previously [7]. On column chromatography, the columns were eluted with petroleum ether (bp 65-71°):ethyl acetate = 4:1, v:v. All solids were recrystallized from boiling ethanol. The uv, ir and ^{1}H nmr spectra were obtained in absolute ethanol, carbon tetrachloride and deuteriochloroform containing 2% of tetramethylsilane, respectively. The mass spectra were recorded at 70 eV on a single focusing Hitachi Perkin-Elmer RMU-6L, or on a double focusing VG Tritech VG TS-250 mass spectrometer. All furoxans and furazans described herein gave the correct molecular ion. Exceptions are noted.

General Procedures for the Preparation of 1,2-Alkylenedioxy-dinitrobenzenes, Azides, Furoxans and Furazans.

A. 1,2-Alkylenedioxydinitrobenzenes.

Into a suspension of the appropriate 1,2-alkylenedioxybenzene derivative and glacial acetic acid kept at 0-10° was added dropwise excess fuming nitric acid (d = 1.52) with periodic cooling by means of an ice-water bath. The mixture was stirred at ambient for 0.5 hour and decanted into ice-water. The solid was collected by suction filtration and washed with a small quantity of cold water.

B. Azides and Furoxans.

A mixture of the appropriate 1,2-alkylenedioxydinitrobenzene and excess sodium azide in dimethyl sulfoxide was stirred at 25-27° for 2-3.5 hours, and decanted into ice-water. The crude azide was isolated by suction filtration and washed with a small quantity of cold water. It was subsequently thermolyzed in refluxing benzene or toluene for 2-3 hours. The solvent was removed *in vacuo* to afford the desired furoxan.

C. Furazans.

The appropriate furoxan (from procedure B) and excess triphenylphosphine in toluene, was heated at reflux for 0.5-3.0 hours. Evaporation of toluene *in vacuo*, gave a mixture which on column chromatography afforded unconverted triphenylphosphine, the desired furazan, and triphenylphosphine oxide in that order of elution.

Exceptions to the general procedures A, B, and C are cited.

Spiro[benzo[1,3]dioxole-2,1'-adamantane] (**11f**) [8].

According to a procedure in the literature [5c], catechol (3.22 g, 29.2 mmoles), adamantanone (4.00 g, 26.6 mmoles) and *p*-toluenesulfonic acid monohydrate (100 mg) in benzene (100 ml), 22 hours, furnished 5.48 g (85%) of **11f**, mp (pale-brown leaflets) 126-127°; ir (potassium bromide): ν 1623 (w), 1598 (w), 1568 (w), 1482 (s), 1363 (m), 1312 (m), 1237 (s), 1104 (s), 1078 (s), 1062 (m), 1013 (s), 903 (s), 808 (m), 742 (s) cm^{-1}; ^{1}H nmr: δ 1.46-2.35 with maxima at 1.81, 2.07, 2.18 (m, 14H), 6.74 (s, 4H); ms: m/z (% relative intensity) 242 ($M^{+\cdot}$, 100), 199 (7), 185 (3), 171 (4), 147 (16), 134 (10), 133 (16), 131 (4), 121 (24), 117 (5), 110 (9), 107 (8), 105 (12), 91 (61), 79 (23), 77 (16), 67 (11), 65 (10), 55 (20), 53 (10), 41 (18).

Anal. Calcd. for $C_{16}H_{18}O_2$: C, 79.31; H, 7.49. Found: C, 79.41; H, 7.36.

2,2-Diethyl-5,6-dinitrobenzo[1,3]dioxole (**12b**).

Benzodioxole **11b** (2.00 g, 11.2 mmoles) [5] and nitric acid (6.0 ml) in acetic acid (5 ml), furnished 2.68 g (89%) of **12b**, mp (pale-yellow needles) 88-89°; ir (chloroform): ν 1603 (w), 1547 (s), 1497 (s), 1397 (m), 1357 (m), 1343 (m), 1276 (s), 1164 (w), 973 (m), 874 (m), 821 (w) cm^{-1}; ^{1}H nmr: δ 0.98 (t, J = 7.5 Hz, 6H), 2.00 (q, J = 7.5 Hz, 4H), 7.17 (s, 2H); ms: m/z (% relative intensity) 268 ($M^{+\cdot}$, 23), 239 (100), 223 (3), 200 (2), 193 (9), 184 (7), 149 (28), 147 (46), 105 (5), 91 (6), 77 (7), 69 (27), 67 (10), 65 (6), 62 (25), 57 (50), 55 (27), 53 (30), 50 (28), 41 (91).

Anal. Calcd. for $C_{11}H_{12}N_2O_6$: C, 49.26; H, 4.51; N, 10.44. Found: C, 49.38; H, 4.44; N, 10.38.

5,6-Dinitrospiro[benzo[1,3]dioxole-2,1'-cyclopentane] (**12c**).

Benzodioxole **11c** (2.00 g, 11.3 mmoles) [5] and nitric acid (5.0 ml) in acetic acid (5 ml), afforded 2.43 g (80%) of **12c**, mp (pale-yellow needles) 132-134°; ir (potassium bromide): ν 1607 (m),

1550 (s), 1537 (s), 1502 (s), 1493 (s), 1393 (m), 1357 (s), 1335 (s), 1279 (s), 1202 (m), 1088 (m), 1022 (w), 957 (w), 888 (m), 823 (m), 753 (m) cm^{-1}; ^1H nmr: δ 1.91 (m, 4H), 2.14 (m, 4H), 7.18 (s, 2H); ms: m/z (% relative intensity) 266 ($M^{+\cdot}$, 72), 265 (9), 237 (89), 192 (3), 191 (3), 174 (4), 173 (9), 146 (12), 145 (38), 132 (6), 77 (6), 67 (95), 62 (20), 55 (19), 51 (36), 50 (100), 41 (94).

Anal. Calcd. for $C_{11}H_{10}N_2O_6$: C, 49.63; H, 3.79; N, 10.52. Found: C, 49.49; H, 3.97; N, 10.26.

5,6-Dinitrospiro[benzo[1,3]dioxole-2,1'-cyclohexane] (**12d**).

Benzodioxole **11d** (2.00 g, 10.5 mmoles) [5] and nitric acid (5.0 ml) in acetic acid (5 ml), gave 2.43 g (82%) of **12d**, mp (pale-yellow leaflets) 120-121°; ir (potassium bromide): ν 1624 (w), 1605 (w), 1550 (s), 1536 (s), 1502 (s), 1494 (s), 1357 (s), 1275 (s), 1143 (m), 1064 (m), 1017 (w), 974 (w), 887 (m), 828 (m), 757 (m) cm^{-1}; ^1H nmr: δ 1.30-2.12 with maximum at 1.93 (m, 10H), 7.18 (s, 2H); ms: m/z (% relative intensity) 280 ($M^{+\cdot}$, 63), 251 (4), 237 (34), 200 (3), 199 (10), 191 (3), 159 (5), 149 (4), 146 (4), 145 (28), 132 (10), 81 (100), 79 (33), 77 (21), 62 (33), 55 (29), 53 (57), 51 (17), 50 (35), 46 (25), 41 (60).

Anal. Calcd. for $C_{12}H_{12}N_2O_6$: C, 51.43; H, 4.32; N, 10.00. Found: C, 51.66; H, 4.30; N, 10.08.

5,6-Dinitrospiro[benzo[1,3]dioxole-2,1'-cycloheptane] (**12e**).

Benzodioxole **11e** (4.00 g, 19.6 mmoles) [5] and nitric acid (7.0 ml) in acetic acid (10 ml), furnished 3.24 g (56%) of **12e**, mp (ethanol at 50°, pale-yellow leaflets) 62-63°; ir (chloroform): ν 1606 (w), 1546 (s), 1497 (s), 1396 (m), 1370 (m), 1336 (m), 1276 (s), 1113 (w), 1057 (w), 990 (w), 913 (w), 872 (m), 819 (w) cm^{-1}; ^1H nmr: δ 1.25-2.49 with maxima at 1.67, 2.16 (m, 12H), 7.17 (s, 2H); ms: m/z (% relative intensity) 294 ($M^{+\cdot}$, 68), 264 (4), 251 (4), 237 (26), 191 (4), 183 (5), 149 (10), 145 (16), 95 (100), 93 (10), 91 (10), 77 (16), 69 (16), 67 (45), 57 (15), 55 (46), 53 (20), 41 (51).

Anal. Calcd. for $C_{13}H_{14}N_2O_6$: C, 53.06; H, 4.80; N, 9.52. Found: C, 52.88; H, 4.87; N, 9.54.

5,6-Dinitrospiro[benzo[1,3]dioxole-2,1'-adamantane] (**12f**).

Benzodioxole **11f** (2.49 g, 10.3 mmoles) and nitric acid (5.0 ml) in acetic acid (5 ml), afforded 3.28 g (96%) of **12f**, mp (pale-yellow needles) 144-147°; ir (chloroform): ν 1606 (w), 1547 (s), 1494 (s), 1453 (w), 1383 (m), 1352 (m), 1337 (m), 1274 (s), 1108 (m), 1082 (m), 1018 (m), 898 (w), 872 (w), 821 (w) cm^{-1}; ^1H nmr: δ 1.45-2.38 with maxima at 1.78, 1.93, 2.21 (m, 14H), 7.23 (s, 2H); ms: m/z (% relative intensity) 332 ($M^{+\cdot}$, 100), 303 (3), 302 (7), 289 (3), 240 (6), 237 (3), 211 (5), 175 (6), 159 (6), 145 (11), 133 (26), 131 (6), 119 (8), 105 (21), 91 (80), 81 (12), 80 (13), 79 (41), 77 (23), 67 (27), 55 (26), 41 (23).

Anal. Calcd. for $C_{16}H_{16}N_2O_6$: C, 57.83; H, 4.85; N, 8.43. Found: C, 57.83; H, 4.77; N, 8.20.

6,6-Dimethyl[1,3]dioxolo[2,3-*f*]-2,1,3-benzoxadiazole 1-Oxide (**14a**).

A mixture of **12a** (0.50 g, 2.1 mmoles) [5], sodium azide (0.54 g, 8.3 mmoles) in dimethyl sulfoxide (9 ml), *ca.* 26°, 3.5 hours, afforded 419 mg of the azide **13a** as a yellow solid, ir: ν 2130 (m), 2110 (s), 1660 (w), 1531 (w), 1480 (s), 1294 (w), 1253 (m), 1240 (m), 1225 (m) cm^{-1}; ^1H nmr δ: 1.73 (s, 6H), 6.62 (s, 1H), 7.39 (s, 1H). Thermolysis of **13a** in refluxing toluene (10 ml), 2 hours followed by column chromatography (benzene) furnished 369 mg (85%) of furoxan **14a**, mp (off-white needles) 185-187°; uv: λ max (ϵ) 369 (10500), 352 (13000), 332 (14000), 317 (12000), 303 sh (8000), 229 (22000) nm; ir (chloroform): ν 1649 (m), 1615 (s), 1589 (s), 1502 (m), 1474 (s), 1397 (s), 1340 (s), 1265 (m), 1135 (m), 1014 (m), 982 (w), 873 (m), 823 (w) cm^{-1}; ^1H nmr: δ 1.73 (s, 6H), 6.41 (br s, 1H), 6.57 (br s, 1H). The absorptions at 6.41 and 6.57 collapsed into a singlet centered at 6.55 after heating the tube at 40-50°.

Anal. Calcd. for $C_9H_8N_2O_4$: C, 51.93; H, 3.87; N, 13.46. Found: C, 51.93; H, 4.00; N, 13.31.

6,6-Diethyl[1,3]dioxolo[2,3-*f*]-2,1,3-benzoxadiazole 1-Oxide (**14b**).

A mixture of **12b** (524 mg, 1.95 mmoles) and sodium azide (509 mg, 7.83 mmoles) in dimethyl sulfoxide (9 ml), *ca.* 27°, 2 hours, afforded 401 mg of the azide **13b** as a yellow solid, ir: ν 2110 (s), 1630 (w), 1619 (w), 1530 (m), 1495 (s), 1463 (w), 1290 (m), 1248 (s), 1054 (w) cm^{-1}; ^1H nmr: δ 0.96 (t, J = 7.5 Hz, 6H), 1.97 (q, J = 7.5 Hz, 4H), 6.62 (s, 1H), 7.39 (s, 1H). Thermolysis of **13b** in refluxing toluene (10 ml) for 2 hours and subsequent column chromatography (benzene) gave 355 mg (77%) of the furoxan **14b**, mp (ethanol at 60°, off-white needles) 79-80°; uv: λ max (ϵ) 369 (10500), 352 (13000), 333 (14500), 318 (13000), 305 sh (9000), 226 (31500) nm; ir: ν 1649 (s), 1614 (s), 1589 (s), 1502 (m), 1478 (s), 1397 (s), 1337 (s), 1257 (w), 1249 (w), 1217 (m), 1136 (m), 1011 (m), 972 (w), 900 (w), 867 (w), 821 (w) cm^{-1}; ^1H nmr: δ 0.96 (t, J = 7 Hz, 6H), 1.98 (q, J = 7 Hz, 4H), 6.40 (br s, 1H), 6.59 (br s, 1H). The latter two absorptions collapsed into a singlet centered at 6.47 on heating the tube at 40-50°.

Anal. Calcd. for $C_{11}H_{12}N_2O_4$: C, 55.93; H, 5.12; N, 11.86. Found: C, 55.95; H, 4.99; N, 11.87.

Spiro[[1,3]dioxolo[2,3-*f*]-2,1'-cyclopentyl]-2,1,3-benzoxadiazole 1-Oxide (**14c**).

A mixture of **12c** (587 mg, 2.21 mmoles) and sodium azide (595 mg, 9.15 mmoles) in dimethyl sulfoxide (9 ml), *ca.* 27°, 2 hours, gave 475 mg of azide **13c** as a pale-yellow solid, ir: ν 2110 (s), 1530 (m), 1494 (s), 1291 (m), 1245 (m), 894 (w) cm^{-1}; ^1H nmr: δ 1.69-2.39 with maxima at 1.93, 2.05, 2.12 (m, 8H), 6.62 (s, 1H), 7.39 (s, 1H). Thermolysis of **13c** in benzene (15 ml) under reflux for 3 hours and subsequent column chromatography (benzene) furnished 423 mg (82%) of furoxan **14c**, mp (pale-yellow leaflets) 156-158°; uv: λ max (ϵ) 369 (8000), 351 (9000), 333 (11000), 318 (9500), 304 sh (6500), 289 sh (3500), 227 (24000), 206 sh (8500) nm; ir: ν 1649 (m), 1618 (s), 1588 (s), 1502 (m), 1479 (s), 1397 (s), 1343 (s), 1222 (m), 1154 (m), 1122 (w), 1090 (w), 1011 (w), 870 (m), 821 (w) cm^{-1}; ^1H nmr: δ 1.68-2.31 with maxima at 1.88, 1.94, 2.05, 2.12 (m, 8H), 6.41 (br s, 1H), 6.57 (br s, 1H). The latter two absorptions collapsed into a singlet centered at 6.50 after heating the tube at 40-50°.

Anal. Calcd. for $C_{11}H_{10}N_2O_4$: C, 56.41; H, 4.30; N, 11.96. Found: C, 56.31; H, 4.18; N, 11.81.

Spiro[[1,3]dioxolo[2,3-*f*]-2,1'-cyclohexyl]-2,1,3-benzoxadiazole 1-Oxide (**14d**).

A mixture of **12d** (587 mg, 2.09 mmoles) and sodium azide (584 mg, 8.98 mmoles) in dimethyl sulfoxide (9 ml), *ca.* 25°, 2.5 hours, afforded 579 mg of the azide **13d** as a pale-yellow solid, ir: ν 2105 (m), 1614 (m), 1527 (w), 1492 (s), 1363 (w), 1146 (w) cm^{-1}; ^1H nmr: δ 1.34-2.13 with maximum at 1.89 (m, 10H), 6.64 (s, 1H), 7.39 (s, 1H). Thermolysis of **13d** in toluene (15 ml) at reflux for 3 hours followed by column chromatography (benzene) furnished 506 mg (97%) of furoxan **14d**, mp (off-white needles) 146-147°; uv: λ max (ϵ) 369 (7000), 351 (9000), 333 (10000), 318 (9000), 304 sh (6000), 289 sh (3000), 217 (17500), 206 sh (7500) nm; ir: ν 1649 (m), 1618

(s), 1588 (m), 1502 (m), 1480 (s), 1398 (s), 1338 (s), 1287 (m), 1244 (m), 1212 (m), 1154 (m), 1127 (m), 1066 (m), 1013 (m), 913 (w), 870 (m), 824 (w) cm^{-1}; ^1H nmr: δ 1.24-2.10 with maximum at 1.88 (m, 10H), 6.41 (br s, 1H), 6.58 (br s, 1H). The latter two absorptions collapsed into a singlet at 6.51 on heating the tube at 40-50°.

Anal. Calcd. for $C_{12}H_{12}N_2O_4$: C, 58.06; H, 4.87; N, 11.28. Found: C, 58.06; H, 4.79; N, 11.21.

Spiro[[1,3]dioxolo[2,3-*f*]-2,1′-cycloheptyl]-2,1,3-benzoxadiazole 1-Oxide (**14e**).

A mixture of **12e** (634 mg, 2.15 mmoles) and sodium azide (536 mg, 8.24 mmoles) in dimethyl sulfoxide (9 ml), *ca.* 27°, 3 hours, gave 560 mg of the azide **13e** as a yellow solid, ir: ν 2110 (s), 1530 (m), 1495 (s), 1430 (s), 1249 (s), 1116 (w), 871 (w) cm^{-1}; ^1H nmr: δ 1.33-2.35 with maxima at 1.68, 2.13 (m, 12H), 6.62 (s, 1H), 7.39 (s, 1H). Thermolysis of **13e** in refluxing benzene (25 ml) for 3 hours, followed by column chromatography (benzene) afforded 506 mg (90%) of the furoxan **14e**, mp (pale-yellow needles) 131-132°; uv: λ max (ε) 369 (8000), 352 (10000), 333 (11500), 318 (10000), 305 sh (7000), 289 sh (3500), 226 (24500) nm; ir: ν 1649 (m), 1614 (s), 1587 (m), 1501 (m), 1482 (s), 1397 (s), 1338 (s), 1258 (m), 1219 (m), 1123 (m), 1061 (m), 1012 (m), 862 (w), 823 (w) cm^{-1}; ^1H nmr: δ: 1.35-2.26 with maxima at 1.68, 2.11 (m, 12H), 6.39 (br s, 1H), 6.57 (br s, 1H). The latter two absorptions collapsed into a singlet at 6.49 after heating the tube at 40-50°.

Anal. Calcd. for $C_{13}H_{14}N_2O_4$: C, 59.54; H, 5.38; N, 10.68. Found: C, 59.62; H, 5.22; N, 10.71.

Spiro[[1,3]dioxolo[2,3-*f*]-2,1′-adamantyl]-2,1,3-benzoxadiazole 1-Oxide (**14f**).

A mixture of **12f** (705 mg, 2.12 mmoles) and sodium azide (545 mg, 8.38 mmoles) in dimethyl sulfoxide (9 ml), *ca.* 27°, 3 hours, gave 645 mg of **13f** as a pale-yellow solid, ir: ν 2110 (s), 1528 (m), 1493 (s), 1452 (w), 1380 (w), 1290 (m), 1247 (s), 1220 (m), 906 (w), 869 (w) cm^{-1}; ^1H nmr: δ 1.44-2.34 with maxima at 1.76, 1.89, 2.00, 2.17 (m, 14H), 6.64 (s, 1H), 7.43 (s, 1H). Thermolysis of **13f** in refluxing toluene (15 ml) for 3 hours and subsequent column chromatography (benzene) furnished 570 mg (89%) of the furoxan **14f**, mp (ethanol:acetone = 1:1, v:v, pale-yellow prisms) 228-229° dec; uv: λ max (ε) 368 (8500), 351 (10500), 334 (12500), 319 (11500), 304 sh (8000), 290 sh (4500), 229 (24500), 207 sh (12000) nm; uv (benzene): λ max (ε) 374 (10000), 356 (12000), 336 (13000), 320 (11000), 305 sh (7500) nm; ir (chloroform): ν 1648 (w), 1613 (s), 1587 (m), 1501 (m), 1474 (s), 1397 (s), 1340 (s), 1257 (w), 1130 (m), 1108 (s), 1083 (m), 1018 (m), 914 (w), 852 (w), 821 (w) cm^{-1}; ^1H nmr: δ 1.62-2.42 with maxima at 1.79, 1.92, 2.07 (m, 14H), 6.40 (br s, 1H), 6.60 (br s, 1H). The latter two absorptions collapsed into a singlet at 6.53 on heating the tube at 40-50°.

Anal. Calcd. for $C_{16}H_{16}N_2O_4$: C, 63.99; H, 5.37; N, 9.33. Found: C, 63.95; H, 5.38; N, 9.30.

[1,3]Dioxolo[2,3-*f*]-2,1,3-benzoxadiazole (**3a**).

A mixture of furoxan **1a** (prepared in two steps from the corresponding dinitro derivative as described above in 91% yield) (308 mg, 1.71 mmoles) [3] and triphenylphosphine (539 mg, 2.05 mmoles) in toluene (6 ml) was heated at reflux for 0.5 hour. Column chromatography (benzene) yielded 172 mg (61%) of the furazan **3a**, mp (pale-yellow granules) 144-145° (closed tube); uv: λ max (ε) 310 sh (8500), 296 (11000), 286 sh (10000), 209 (6000) nm; ir (chloroform): ν 1610 (m), 1502 (m), 1490 (s), 1395 (w), 1360 (s), 1196 (w), 1120 (w), 1041 (m), 991 (w), 967 (m), 887 (w), 829 (m) cm^{-1}; ^1H nmr: δ 6.11 (s, 2H), 6.89 (s, 2H).

Anal. Calcd. for $C_7H_4N_2O_3$: C, 51.23; H, 2.46; N, 17.07. Found: C, 51.18; 2.47; N, 16.98.

[1,3]Dioxolo[2,3-*e*]-2,1,3-benzoxadiazole (**4a**).

A mixture of furoxan **2a** (88 mg, 0.49 mmole) [2a] and triphenylphosphine (165 mg, 0.629 mmole) in toluene (5 ml) was heated at reflux for one hour. Column chromatography (benzene) afforded 72 mg (90%) of furazan **4a**, mp (yellow granules) 98-100°; uv: λ max (ε) 393 (3500), 299 sh (1000), 284 (1500), 227 (22500) nm; ir (chloroform): ν 1649 (m), 1574 (m), 1524 (w), 1410 (m), 1402 (m), 1380 (m), 1264 (s), 1090 (s), 1065 (m), 1045 (m), 1020 (m), 999 (m), 910 (w) cm^{-1}; ^1H nmr: δ 6.23 (s, 2H), 7.26 (d, J = 9.5 Hz, 1H), 7.52 (d, J = 9.5 Hz, 1H).

Anal. Calcd. for $C_7H_4N_2O_3$: C, 51.23; H, 2.46; N, 17.07. Found: C, 51.38; H, 2.69; N, 17.15.

6,7-Dihydro[1,4]dioxino[2,3-*f*]-2,1,3-benzoxadiazole (**3b**).

A mixture of furoxan **1b** (205 mg, 1.06 mmoles) [2b,3] and triphenylphosphine (339 mg, 1.29 mmoles) in toluene (5 ml) was heated at reflux for 0.5 hour. Column chromatography (benzene) gave 180 mg (96%) of furazan **3b**, mp (off-white needles) 200-201° (closed tube); uv: λ max (ε) 315 sh (7500), 303 (8000), 292 sh (6500), 213 (10500) nm; ir (chloroform): ν 1500 (s), 1459 (w), 1412 (w), 1397 (w), 1340 (s), 1272 (w), 1175 (vw), 1065 (m), 999 (m), 937 (w), 912 (w), 879 (m), 838 (m) cm^{-1}; ^1H nmr: δ 4.36 (s, 4H), 7.10 (s, 2H).

Anal. Calcd. for $C_8H_6N_2O_3$: C, 53.94; H, 3.39; N, 15.72. Found: C, 54.08; H, 3.28; N, 15.88.

7,8-Dihydro[1,4]dioxino[2,3-*e*]-2,1,3-benzoxadiazole (**4b**).

A mixture of furoxan **2b** (56 mg, 0.29 mmole) [2a] and triphenylphosphine (117 mg, 0.446 mmole) in toluene (2 ml) was heated at reflux for one hour. Column chromatography yielded 48 mg (93%) of furazan **4b**, mp (pale-yellow needles) 133-135°; uv: λ max (ε) 362 (2500), 293 sh (1500), 281 (2500), 271 sh (2000), 221 (17000) nm; ir (chloroform): ν 1635 (m), 1566 (s), 1542 (w), 1471 (s), 1371 (m), 1277 (s), 1254 (m), 1237 (m), 1182 (w), 1118 (s), 1100 (s), 985 (s), 907(w), 888 (w) cm^{-1}; ^1H nmr: δ 4.42 (s, 4H), 7.06 (d, J = 9.5 Hz, 1H), 7.33 (d, J = 9.5 Hz, 1H).

Anal. Calcd. for $C_8H_6N_2O_3$: C, 53.94; H, 3.39;N, 15.72. Found: C, 53.99; H, 3.50; N, 15.81.

8,9-Dihydro-7*H*-[1,4]dioxepino[2,3-*e*]-2,1,3-benzoxadiazole (**4c**).

A mixture of furoxan **2c** (81 mg, 0.39 mmole) [2a] and triphenylphosphine (133 mg, 0.507 mmole) in toluene (3 ml) was heated at reflux for one hour. Column chromatography (benzene) furnished 70 mg (94%) of furazan **4c**, mp (pale-yellow needles) 111-113°; uv: λ max (ε) 348 (3500), 292 sh (2500), 281 (3500), 271 sh (3000), 219 (20000) nm; ir (chloroform): ν 1625 (m), 1550 (s), 1468 (m), 1459 (m), 1316 (m), 1231 (m), 1115 (s), 1062 (m), 995 (s) cm^{-1}; ^1H nmr: δ 2.32 (qn, J = 6 Hz, 2H), 4.41 (t, J = 6 Hz, 2H), 4.49 (t, J = 6 Hz, 2H), 7.07 (d, J = 9 Hz, 1H), 7.34 (d, J = 9 Hz, 1H).

Anal. Calcd. for $C_9H_8N_2O_3$: C, 56.25; H, 4.20; N, 14.58. Found: C, 56.08; H, 4.11; N, 14.38.

8,9-Dihydro-7*H*-4-nitro[1,4]dioxepino[2,3-*e*]-2,1,3-benzoxadiazole (**10c**).

A mixture of furoxan **9** (107 mg, 0.423 mmole) [2a] and triphenylphosphine (122 mg, 0.465 mmole) in toluene (4 ml) was heated at reflux for 0.5 hour. Column chromatography (benzene) afford-

ed 93 mg (94%) of the title furazan, mp (pale-yellow granules) 124-125°; uv: λ max (ε) 348 (2500), 292 sh (2000), 262 (5500), 223 (12000) nm; ir (chloroform): ν 1627 (w), 1548 (s), 1472 (m), 1459 (m), 1381 (m), 1368 (m), 1344 (m), 1316 (m), 1268 (w), 1172 (m), 1082 (s), 1026 (w), 1007 (w), 982 (vw), 892 (w), 857 (w), 813 (vw) cm^{-1}; ^1H nmr: δ 2.40 (qn, J = 6 Hz, 2H), 4.44 (t, J = 6 Hz, 2H), 4.59 (t, J = 6 Hz, 2H), 7.76 (s, 1H).

Anal. Calcd. for $C_9H_7N_3O_5$: C, 45.58; H, 2.97; N, 17.72. Found: C, 45.64; H, 2.97; N, 17.76.

7,8,9,10-Tetrahydro-6*H*-[1,4]dioxonino[2,3-*f*]-2,1,3-benzoxadiazole (**3e**).

A mixture of furoxan **1e** (127 mg, 0.538 mmole) [2a] and triphenylphosphine (157 mg, 0.599 mmole) in toluene (3 ml) was heated at reflux for one hour. Column chromatography gave 109 mg (92%) of furazan **3e**, mp (white granular plates or needles) 89-90°; uv: λ max (ε) 299 sh (8500), 291 (9000), 211 (19500) nm; ir: ν 1495 (s), 1444 (w), 1333 (s), 1212 (s), 1188 (s), 1166 (m), 1017 (m), 1004 (s), 969 (m), 920 (m), 880 (m), 852 (m) cm^{-1}; ^1H nmr: δ 1.89 (m, 6H), 4.30 (m, 4H), 7.27 (s, 2H).

Anal. Calcd. for $C_{11}H_{12}N_2O_3$: C, 59.99; H, 5.49; N, 12.72. Found: C, 60.11; H, 5.38; N, 12.81.

8,9,10,11-Tetrahydro-7*H*-[1,4]dioxonino[2,3-*e*]-2,1,3-benzoxadiazole (**4e**).

A mixture of furoxan **1e** (123 mg, 0.521 mmole) [2a] and triphenylphosphine (154 mg, 0.587 mmole) in toluene (4 ml) was heated at reflux for 1.5 hours. Column chromatography yielded 108 mg (94%) of furazan **4e**, mp (ethanol at 50°, off-white needles) 54-55°; uv: λ max (ε) 345 (2000), 292 sh (1500), 279 (2500), 270 sh (2000), 216 (13000) nm; ir: ν 1627 (m), 1548 (m), 1475 (m), 1367 (m), 1319 (m), 1235 (s), 1109 (m), 992 (s), 889 (m) cm^{-1}; ^1H nmr: δ 1.84 (m, 6H), 4.45 (t, J = 5 Hz, 2H), 4.64 (t, J = 5 Hz, 2H), 7.05 (d, J = 9.5 Hz, 1H), 7.38 (d, J = 9.5 Hz, 1H).

Anal. Calcd. for $C_{11}H_{12}N_2O_3$: C, 59.99; H, 5.49; N, 12.72. Found: C, 59.94; H, 5.48; N, 12.88.

6,7,8,9,10,11-Hexahydro[1,4]dioxecino[2,3-*f*]-2,1,3-benzoxadiazole (**3f**).

A mixture of furoxan **1f** (127 mg, 0.507 mmole) [2a] and triphenylphosphine (154 mg, 0.587 mmole) in toluene (3 ml) was heated at reflux for 45 minutes. Column chromatography furnished 101 mg (85%) of furazan **3f**, mp (ethanol at 70°, white needles) 87-88°; uv: λ max (ε) 327 sh (3000), 289 (9000), 208 (19000) nm; ir: ν 1502 (s), 1467 (w), 1404 (w), 1336 (s), 1225 (s), 1172 (w), 1161 (w), 1005 (m), 954 (w), 924 (w), 874 (m), 861 (w) cm^{-1}; ^1H nmr: δ 1.74 (m, 8H), 4.19 (m, 4H), 7.14 (s, 2H).

Anal. Calcd. for $C_{12}H_{14}N_2O_3$: C, 61.53; H, 6.02; N, 11.96. Found: C, 61.56; H, 6.00; N, 11.86.

7,8,9,10,11,12-Hexahydro[1,4]dioxecino[2,3-*e*]-2,1,3-benzoxadiazole (**4f**).

A mixture of furoxan **2f** (198 mg, 0.791 mmole) [2a] and triphenylphosphine (228 mg, 0.869 mmole) in toluene (4 ml) was heated at reflux for 1.5 hours. Column chromatography afforded 177 mg (95%) of furazan **4f**, mp (ethanol at 50° then −20°, white solid) 53-55°; uv: λ max (ε) 347 (2500), 292 sh (1500), 281 (2000), 272 sh (2000), 214 (14000) nm; ir: ν 1623 (m), 1535 (s), 1446 (s), 1365 (m), 1322 (m), 1250 (m), 1228 (s), 1176 (m), 1110 (s), 1080 (w), 1058 (m), 1006 (s), 974 (m), 918 (w), 889 (m) cm^{-1}; ^1H nmr: δ 1.73 (s, 8H), 4.27 (t, J = 4.5 Hz, 2H), 4.57 (t, J = 4.5 Hz, 2H), 7.22 (d, J = 9.5 Hz, 1H), 7.50 (d, J = 9.5 Hz, 1H).

Anal. Calcd. for $C_{12}H_{14}N_2O_3$: C, 61.53; H, 6.02; N, 11.96. Found: C, 61.68; H, 6.19; N, 12.11.

5,6-Dimethoxy-2,1,3-benzoxadiazole (**6**) [4].

A mixture of furoxan **5** (207 mg, 1.06 mmoles) [3] and triphenylphosphine (423 mg, 1.61 mmoles) in toluene (5 ml) was heated at reflux for one hour. Column chromatography (chloroform) gave 142 mg (75%) of furazan **6**, mp (white needles) 195-196° (closed tube) (lit [4] mp 178-181°); uv: λ max (ε) 307 sh (3500), 292 (5000), 284 sh (4500), 207 (8000) nm; ir (chloroform): ν 1634 (m), 1543 (m), 1516 (s), 1462 (m), 1362 (s), 1169 (m), 1004 (m), 853 (m), 815 (w) cm^{-1}; ^1H nmr: identical to that reported [4].

Anal. Calcd. for $C_8H_8N_2O_3$: C, 53.33; H, 4.48; N, 15.55. Found: C, 53.44; H, 4.61; N, 15.68.

4,5-Dimethoxy-2,1,3-benzoxadiazole (**8**).

A mixture of furoxan **7** (71 mg, 0.36 mmole) [9] and triphenylphosphine (123 mg, 0.469 mmole) in toluene (4 ml) was heated at reflux for one hour. Column chromatography (benzene) yielded 63 mg (97%) of furazan **8**, mp (ethanol at 50°, yellow granular plates) 43-44°; uv: λ max (ε) 354 (2000), 292 sh (1500), 280 (2000), 272 sh (1500), 261 sh (1500), 254 sh (1000), 215 (12000) nm; ir: ν 1624 (m), 1543 (s), 1536 (s), 1460 (s), 1430 (m), 1368 (w), 1327 (s), 1262 (m), 1242 (s), 1210 (m), 1171 (m), 1126 (m), 1111 (s), 1055 (m), 1010 (s), 983 (s), 892 (m) cm^{-1}; ^1H nmr: δ 4.00 (s, 3H), 4.25 (s, 3H), 7.26 (d, J = 9.5 Hz, 1H), 7.47 (d, J = 9.5 Hz, 1H).

Anal. Calcd. for $C_8H_8N_2O_3$: C, 53.33; H, 4.48; N, 15.55. Found: C, 53.54; H, 4.60; N, 15.56.

6,6-Dimethyl[1,3]dioxolo[2,3-*f*]-2,1,3-benzoxadiazole (**15a**).

A mixture of furoxan **14a** (178 mg, 0.855 mmole) and triphenylphosphine (298 mg, 1.14 mmoles) in toluene (5 ml) was heated at reflux for 1.5 hours. Column chromatography (benzene) furnished 132 mg (80%) of furazan **15a**, mp (white granular plates) 198-200° (closed tube); uv: λ max (ε) 308 sh (10500), 296 (14000), 287 sh (12500), 223 sh (2500), 207 (9000) nm; ir (chloroform): ν 1605 (m), 1492 (s), 1389 (m), 1381 (m), 1364 (s), 1229 (m), 1086 (w), 999 (s), 979 (w), 856 (s), 824 (m) cm^{-1}; ^1H nmr: δ 1.76 (s, 6H), 6.81 (s, 2H).

Anal. Calcd. for $C_9H_8N_2O_3$: C, 56.25; H, 4.20; N, 14.58. Found: C, 56.23; H, 4.39; N, 14.34.

6,6-Diethyl[1,3]dioxolo[2,3-*f*]-2,1,3-benzoxadiazole (**15b**).

A mixture of furoxan **14b** (220 mg, 0.931 mmole) and triphenylphosphine (520 mg, 1.98 mmoles) in toluene (5 ml) was heated at reflux for 3 hours. Column chromatography (benzene) afforded 134 mg (65%) of furazan **15b**, mp (ethanol at 50°, white granular plates) 61-62°; uv: λ max (ε) 311 sh (10500), 297 (15000), 287 sh (13000), 230 sh (2000), 208 (12000) nm; ir: ν 1605 (m), 1494 (s), 1462 (m), 1366 (s), 1220 (s), 1164 (w), 1053 (w), 998 (s), 903 (m), 853 (m), 822 (m) cm^{-1}; ^1H nmr: δ 0.97 (t, J = 7.5 Hz, 6H), 2.00 (q, J = 7.5 Hz, 4H), 6.80 (s, 2H).

Anal. Calcd. for $C_{11}H_{12}N_2O_3$: C, 59.99; H, 5.49; N, 12.72. Found: C, 59.88; H, 5.49; N, 12.70.

Spiro[[1,3]dioxolo[2,3-*f*]-2,1′-cyclopentyl]-2,1,3-benzoxadiazole (**15c**).

A mixture of furoxan **14c** (201 mg, 0.858 mmole) and triphenyl-

phosphine (342 mg, 1.30 mmoles) in toluene (6 ml) was heated at reflux for one hour. Column chromatography (benzene) gave 139 mg (74%) of furazan **15c**, mp (white leaflets) 159-160°; uv: λ max (ε) 311 sh (9500), 299 (13500), 287 sh (12000), 275 sh (7000), 233 sh (2000), 207 (135000) nm; ir: ν 1606 (m), 1494 (s), 1364 (s), 1219 (s), 1202 (m), 1094 (m), 998 (s), 858 (s), 823 (m) cm^{-1}; ^1H nmr: δ 1.71-2.32 with maxima at 1.86, 1.89, 1.92, 1.97, 2.07, 2.09, 2.15, 2.22 (m, 8H), 6.81 (s, 2H).

Anal. Calcd. for $C_{11}H_{10}N_2O_3$: C, 60.55; H, 4.62; N, 12.84. Found: C, 60.81; H, 4.87; N, 13.01.

Spiro[[1,3]dioxolo[2,3-*f*]-2,1'-cyclohexyl]-2,1,3-benzoxadiazole (**15d**).

A mixture of furoxan **14d** (201 mg, 0.810 mmole) and triphenylphosphine (332 mg, 1.27 mmoles) in toluene (6 ml) was heated at reflux for one hour. Column chromatography (benzene) yielded 143 mg (76%) of furazan **15d**, mp (white leaflets) 149-150°; uv: λ max (ε) 311 sh (10500), 298 (15000), 288 sh (13000), 276 (sh (8000), 231 sh (2000), 208 (13500) nm; ir: ν 1606 (m), 1494 (s), 1449 (m), 1371 (s), 1359 (s), 1281 (m), 1218 (s), 1201 (m), 1139 (m), 1067 (s), 999 (s), 917 (m), 857 (s), 823 (m) cm^{-1}; ^1H nmr: δ 1.19-2.21 with maximum at 1.88 (m, 10H), 6.79 (s, 2H).

Anal. Calcd. for $C_{12}H_{12}N_2O_3$: C, 62.06; H, 5.21; N, 12.06. Found: C, 62.19; H, 5.13; N, 11.91.

Spiro[[1,3]dioxolo[2,3-*f*]-2,1'-cycloheptyl]-2,1,3-benzoxadiazole (**15e**).

A mixture of furoxan **14e** (224 mg, 0.854 mmole) and triphenylphosphine (342 mg, 1.30 mmoles) in toluene (6 ml) was heated at reflux for one hour. Column chromatography (benzene) furnished 156 mg (74%) of furazan **15e**, mp (white leaflets) 122-123°; uv: λ max (ε) 312 sh (10000), 298 (13500), 288 sh (12000), 275 sh (7500), 231 sh (2500), 207 (14000) nm; ir: ν 1603 (w), 1492 (s), 1373 (m), 1359 (s), 1215 (m), 1114 (w), 1059 (w), 999 (m), 847 (w), 821 (w) cm^{-1}; ^1H nmr: δ 1.33-2.32 with maxima at 1.70, 2.13 (m, 12H), 6.81 (s, 2H).

Anal. Calcd. for $C_{13}H_{14}N_2O_3$: C, 63.40; H, 5.73; N, 11.38. Found: C, 63.58; H, 5.81; N, 11.48.

Spiro[[1,3]dioxolo[2,3-*f*]-2,1'-adamantyl]-2,1,3-benzoxadiazole (**15f**).

A mixture of furoxan **14f** (198 mg, 0.659 mmole) and triphenylphosphine (266 mg, 1.01 mmoles) in toluene (6 ml) was heated at reflux for one hour. Column chromatography (benzene) afforded 148 mg (79%) of furazan **15f**, mp (ethanol:acetone = 1:1, v:v, white leaflets) 243-245° (closed tube); uv: λ max (ε) 314 sh (12500), 300 (18000), 290 sh (15500), 276 sh (9000), 232 sh (2500), 208 (14000) nm; ir (chloroform): ν 1607 (m), 1493 (s), 1386 (m), 1369 (s), 1359 (s), 1108 (m), 1084 (m), 994 (m), 916 (w), 842 (m), 821 (w) cm^{-1}; ^1H nmr: δ 1.41-2.36 with maxima at 1.79, 1.92, 2.11 (m, 14H), 6.84 (s, 2H).

Anal. Calcd. for $C_{16}H_{16}N_2O_3$: C, 67.59; H, 5.67; N, 9.85. Found: C, 67.52; H, 5.81; N, 10.01.

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