PROPERTIES OF FUROXANS MONOSUBSTITUTED WITH ADAMANTANES

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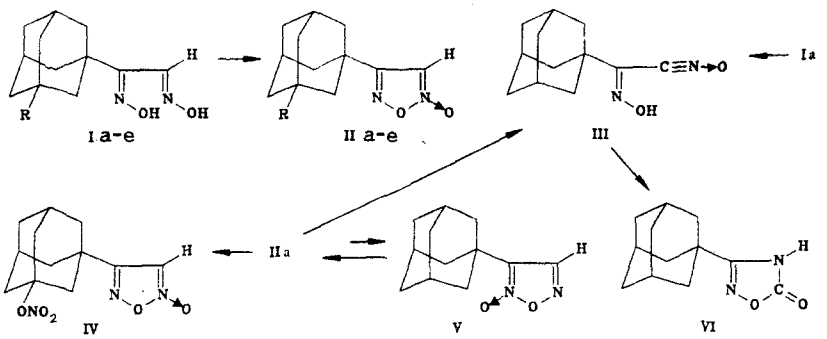
Furoxans monosubstituted with a series of adamantanes have been obtained by oxidation of anti-[1-(3-R-adamantyl)]-amphi-glyoximes. Depending on the conditions 4-(1-adamantyl)furoxan is partially isomerized to 3-(1-adamantyl)furoxan or by increasing the time of boiling and concentration of furoxan in p-xylene is isomerized to the thermodynamically stable 3-(1-adamantyl)-1,2,4-oxadiazol-5-one.

As a continuation of our investigations into the chemical conversions of anti-[1-(3-R-adamantyl)]-amphi-glyoximes (Ia-e) [1] we have studied the possibility of forming heterocycles from them.

It was found that when glyoximes Ia-e are oxidized with 1.2 moles of nitric acid (d 1.5) in 60-80 moles of glacial acetic acid, 4-[1-(3-R-adamantyl)]furoxans (IIa-e) are readily formed. The use of 4 N or 8 N nitric acid [2] as oxidizing agent leads to a reduction in the rate of formation of furoxan IIa.

In the IR spectra of the compounds synthesized IIa-e there are several bands characteristic of monosubstituted furoxans [3]: 3180-3150, 1635-1610, 1365, 1188-1170, 990, 945, 930 cm^{-1}.



I—IIa R=H, b R=CH_3, c R=Cl, d R=OH, e R=$C_6H_4CH_3$-*p*

It should be noted that when furoxan IIa was boiled with carbon, appreciable ring opening occurred during recrystallization to give 2-(1-adamantyl)-2-hydroxyiminoacetonitrile oxide (III), which was indicated by the appearance in the IR spectrum of the recrystallized product of a characteristic intense absorption band in the region of 2295 cm^{-1} assigned to the nitrile oxide group. Introduction of an adamantyl substituent into the furoxan ring makes furoxan IIa stable in acetone solution unlike 4-phenylfuroxan, which when dissolved in acetone is readily isomerized to 2-phenyl-2-hydroxyiminoacetonitrile oxide [4]. The furoxan ring remains stable in concentrated nitric acid — when compound IIa is treated with excess nitric acid (d 1.5) 4-[1-(3-nitroxyadamantyl)]furoxan (IV) is formed. We have developed a method that is simple in the preparative sense for obtaining compound III in sufficient quantity for a study of its properties and behavior during isomerization. It is known [5] that by oxidizing phenylglyoxime with an ammonia solution of $K_3Fe(CN)_6$ to 3-amino-4-phenylfuroxan, 2-phenyl-2-hydroxyiminoacetonitrile oxide is formed as an intermediate. It has been found that oxidation of an ether solution of glyoxime Ia with 2.5 moles of an alkaline solution of $K_3Fe(CN)_6$ for 2 h at 20°C can give compound III in high yield, and its structure is confirmed by the data of its IR and PMR spectra. In the PMR spectrum of compound III there is one signal from the proton of the hydroxyimino group at 11.50 ppm.

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TABLE 1. PMR Spectra* of Compounds Synthesized

Compound	Chemical shift, δ, ppm	
	3-R—Ad	signal from proton of functional group
IIa	1,75—2,08 (15H, m, Ad)	7,68 (1H, s, CH=N)
IIb	0,88 (3H, s, CH_3), 1,53—2,08 (14H, m, Ad)	7,65 (1H, s, CH=N)
IIc	1,68—2,41 (14H, m, Ad)	7,75 (1H, s, CH=N)
IId	1,62—2,26 (14H, m, Ad), 3,65 (1H, s, OH)	7,72 (1H, s, CH=N)
IIe	1,82—2,08 (14H, m, Ad), 2,27 (3H, s, CH_3), 7,05—7,35 (4H, m, Ar)	7,77 (1H, s, CH=N)
III	1,67—2,00 (15H, m, Ad)	11,50 (1H, s, C=NOH)
IV	1,77—2,41 (14H, m, Ad)	7,80 (1H, s, CH=N)
V	1,79—2,06 (14H, m, Ad)	8,54 (1H, s, CH=N)
VI	1,75—2,05 (15H, m, Ad)	10,82 (NH)

*Solvent for compounds IIa-e, III, IV, and V with acetone-d_6, and $CDCl_3$ for compound VI.

TABLE 2. Properties of Compounds IIa-e, III-VI

Compound	T_{mp} °C	R_f*	Found, %			Empirical formula	Calculated, %			Yield, %
			C	H	N		C	H	N	
IIa	127—128 (hexane)	0,46	65,7	7,5	12,9	$C_{12}H_{16}N_2O_2$	65,4	7,3	12,7	63
IIb	74—77 (pentane)	0,35	66,9	7,9	12,2	$C_{13}H_{18}N_2O_2$	66,6	7,7	12,0	60
IIc	132—134 (ether—pentane)	0,40	56,9	5,9	10,8	$C_{12}H_{15}ClN_2O_2$	56,6	5,9	11,0	68
IId	163—164 (decomp.) (hexane—ethyl acetate)	0,41	60,7	6,5	12,0	$C_{12}H_{16}N_2O_3$	61,0	6,8	11,9	60
IIe	105—106 (pentane)	0,26	73,4	7,2	9,2	$C_{19}H_{22}N_2O_2$	73,5	7,1	9,0	71
III	151—153 (decomp.)	0,56	65,6	7,5	12,9	$C_{12}H_{16}N_2O_2$	65,4	7,3	12,7	71
IV	117—119 (chloroform—pentane)	0,30	51,6	5,6	15,2	$C_{12}H_{15}N_3O_5$	51,2	5,4	14,9	78
V	165—167	0,37	65,8	7,5	12,9	$C_{12}H_{16}N_2O_2$	65,4	7,3	12,7	22
VI	227—229 (toluene)	0,19	65,5	7,4	12,9	$C_{12}H_{16}N_2O_2$	65,4	7,3	12,7	63

*In the solvent system CCl_4—acetone in the ratio: 60:1 for IIa, b, e and V; 6:0.5 for IIc and IV; 6:3 for IId; 6:1 for III and VI.

In order to determine the position of the exocyclic oxygen in furoxans IIa-e, the isomerization of furoxan IIa, which contains an unsubstituted adamantane fragment, was carried out in p-xylene.

According to the results of [2] isomerization of 4-phenylfuroxan as a 10% solution in p-xylene gives only 3-phenylfuroxan.

We have found that by boiling 4-(1-adamantyl)furoxan IIa as a 1% solution in p-xylene for 2 h a mixture of isomers IIa (78%) and V (22%) is formed, according to the PMR data. It should be noted that chromatographic separation of the mixture of isomers IIa and V on silica gel led to the isolation of hydroxyiminoacetonitrile oxide III, which is caused by opening of the furoxan ring of IIa under these conditions.

In the IR spectrum of furoxan V the band with the highest intensity, corresponding to vibrations of the furoxan ring, is displaced to lower frequency (1590 cm^{-1}) in comparison with furoxan IIa (1610 cm^{-1}). In the PMR spectra of furoxans IIa-e the $C_{(3)}$-H signal is displaced upfield by 0.74-0.89 ppm (Table 1) relative to the $C_{(4)}$-H signal in furozan V, which is due to the shielding effect of the exocyclic oxygen [2, 3].

When furoxan IIa as a 10% solution in p-xylene is boiled for 13 h 3-(1-admantyl)-1,2,4-oxadiazol-5-one (VI) is obtained in 50% yield. The course of the isomerization was monitored by TLC until the complete disappearance of furoxan IIa and hydroxyiminoacetonitrile oxide III.

In the PMR spectrum of compound VI in $CDCl_3$ there is a weak broad signal due to NH at 10.82 ppm. In the IR spectrum of oxadiazolone VI there are several bands characteristic of this particular structure [4]: 3150, 1765, 1580, 1240, 980, 960, 890 cm^{-1}.

The formation of oxadiazolone VI under the conditions indicated above is due to the possible thermal ring opening of monosubstituted furoxan IIa to hydroxyiminoacetonitrile oxide III, which by analogy with 2-phenyl-2-hydroxyiminoacetonitrile oxide [6, 7] when boiled in xylene undergoes an isocyanate rearrangement with subsequent cyclization to oxadiazolone VI. Cyclization to oxadiazolone VI in 63% yield also occurs by prolonged boiling of compound III in toluene.

EXPERIMENTAL

IR spectra were recorded on a IKS-22 spectrometer in the form of KBr pellets; PMR spectra were recorded on a Bruker WP-80 DS instrument (80 MHz) with HMDS as internal standard. Chemapol 100-400 silica gel was used for chromatographic purification and separation of isomers. The course of the reactions and the purity of the compounds obtained were monitored by means of TLC on Silufol UV-254 plates.

anti-[1-(3-R-Adamantyl)]-amphi-glyoximes (Ia-d). These were used [1] after chromatographic purification of the starting materials in a CCl_4-acetone (6:2) system for compounds Ia-c, e and a CCl_4-acetone (6:4) system for compound Id followed by recrystallization from the appropriate solvents.

The properties of the compounds IIa-e, III-VI obtained are given in Table 2.

4-(1-Adamantyl)furoxan (IIa). A. To 0.46 ml (10.8 mmole) of nitric acid (d 1.5) in 36 ml (629.3 mmole) of glacial acetic acid with agitation at 22°C was added in such a way as to limit the formation of oxide 2 g (8.9 mmole) of anti-(1-adamantyl)-amphi-glyoxime (Ia) ground to a powder. The reaction mixture was agitated for 30 min and poured into ice. The precipitate was filtered off, washed with water, and dried. After recrystallization without using carbon 1.25 g of furoxan IIa was obtained from hexane.

4-[1-(3-Methyladamantyl)]furoxan (IIb) and 4-[1-(3-p-tolyladamantyl)]furoxan (IIc) were obtained in a similar manner. In the preparation of 4-[1-(3-chloroadamantyl)] furoxan (IIc) the reaction mixture was heated to 36°C in order to dissolve the material completely. In the preparation of 4-[1-(3-hydroxyadamantyl)]furoxan (IId) the acidic aqueous solution remaining after separation of precipitate was also extracted with ether and the reaction product recrystallized.

B. To 20 ml of 8 N nitric acid was added with agitation 1 g (4.5 mmole) of glyoxime Ia. The suspension was agitated for 5-8 h at 25°C and left to stand for 12 h. The precipitate was filtered off, washed with water, and dried. After recrystallization 0.54 g of furoxan IIa with mp 123-126°C was obtained.

Isomerization of 4-(1-Adamantyl)furoxan (IIa). A. To 0.8 g of furoxan IIa was added 92 ml of p-xylene and the mixture was boiled for 2 h. The solvent was removed under vacuum and the residue (a mixture of isomers IIa and V, 3.5:1, according to PMR) was chromatographed on a 1.5 × 100 cm column with CCl_4-acetone (60:1) as eluant. This gave 0.12 g (16%) of furoxan V and 0.35 g (44%) of a mixture of furoxans V and IIa. The column was eluted with CCl_4-acetone (6:1) and 0.25 g (31%) of hydroxyiminoacetonitrile oxide III was isolated. IR spectrum: 3210 (OH), 2295 (C≡N → O), 1600 cm^{-1} (C=N).

B. To 0.8 g of furoxan IIa was added 9 ml of p-xylene and the mixture was boiled for 13 h; on cooling 0.4 g (50%) of 3-(1-adamantyl)-1,2,4-oxadiazol-5-one (VI) precipitated out.

2-(1-Adamantyl)-2-hydroxyiminoacetonitrile Oxide (III). To a solution of 2 g (9 mmole) of glyoxime Ia in 60 ml of ether was added dropwise with agitation a solution of 7.4 g (22.5 mmole) of $K_3Fe(CN)_6$ and 1.26 g (22.5 mmole) of KOH in 67 ml of water. The reaction mixture was agitated for 2 h at 20-25°C and the ether layer was separated, washed with water, and dried. After evaporation of the ether the residue was washed with pentane, and 1.4 g (71%) of compound III was obtained with mp 147-149°C (decomp.). After chromatographic purification (eluant was CCl_4–acetone, 6:1), mp 151-153°C (decomp.).

3-(1-Adamantyl)-1,2,4-oxadiazol-5-one (VI). To 0.7 g of compound III was added 60 ml of toluene and the mixture was boiled for 10 h; the excess solvent was distilled off and the precipitate of compound VI filtered off.

4-[1-(3-Nitroxyadamantyl)]furoxan (IV). To 9.5 ml (227 mmole) of nitric acid (d 1.5) at 26°C and with agitation was added 0.5 g (2 mmole) of 4-(1-adamantyl)furoxan IIa, and the mixture was left to stand for 2 h. The reaction mixture was poured into ice and the precipi-

tate (0.5 g) of compound IV was filtered off. IR spectrum: 3180, 2940, 1610, 1440, 1415, 1300, 1290, 1215, 890, 870 cm^{-1}.

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SYNTHESIS AND SPECTRAL LUMINESCENCE PROPERTIES OF DIBENZO[b,i]PHENOXAZINE AND SEVERAL OF ITS DERIVATIVES

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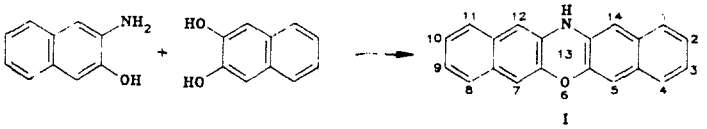
The synthesis of dibenzo[b,i]phenoxazine, its p-tert-butyl substituted analog, and a series of nitro-, amino-, and bromosubstituted derivatives, is described. The spectral luminescence properties of these newly synthesized compounds have been investigated.

Phenoxazine derivatives, in particular hydroxy- and aminophenoxazines, are efficient red heat (light) luminophores, and are thus widely used as generating compounds in tunable visible region lasers [1]. We have previously demonstrated [2] that 3,6-dinitrophenoxazine, in contrast to the majority of other nitro compounds, also exhibits luminescence in alkaline alcohol solutions (luminescence λ_{max} 760 nm). This may be rationalized in terms of its deprotonation to form a symmetrical anion which is an analog of phenoxazine dyes, except that it carries a negative charge. In this regard, therefore, it was of interest to us to study condensed phenoxazine analogs, especially its linearly annelated naphthalene analog, dibenzo[b,i]phenoxazine (I).

In the present paper we describe the synthesis and spectral luminescence properties of compound I and a series of its derivatives. Compound I was first reported as a side product (~2% yield) in the synthesis of 2,2'-binaphth[2,3-d]oxazole from 3-amino-2-naphthol and anhydrous oxalic acid, but was not adequately characterized [3]. We have prepared compound I, in analogy with phenoxazine [4], by treatment of 3-amino-2-naphthol with 2,3-dihydronaphthalene, with an overall yield of about 45%.



I

The electronic absorption spectrum of compound I in DMF contains, in addition to the two bands reported in [3], with maxima at 328 and 385 nm, another band with an absorption maximum at 278 nm.

The PMR spectrum of compound I (in DMSO-D_6) exhibits two broadened singlets at 6.74 and 7.08 ppm, corresponding to the protons at $C_{(12)}$ ($C_{(14)}$) and $C_{(5)}$ ($C_{(7)}$). The $C_{(1)}$($C_{(11)}$)

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