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TETRAHEDRON

Nucleophilic Attack on the Nitrone Tautomeric Form of 1-Hydroxy-2-Phenylindole

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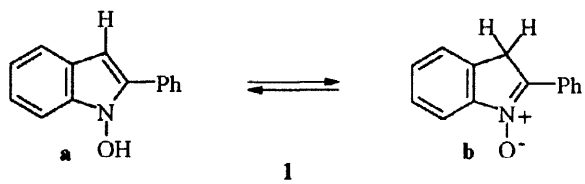
Abstract. 1-Hydroxy-2-phenylindole exists in solution in both hydroxylamine and nitrone tautomeric forms: the latter is able to add organometallic compounds, forming stable indolinic aminoxyls, which were also prepared for comparison by an independent way. The title compound, after irradiation with a mercury lamp lead to a spin adduct, whose identification was proved by deuteration of 1-hydroxy-2-phenylindole at different levels. A mechanism similar to that invoked in the photoreaction of phenyl-*tert*-butylnitrone with nucleophiles has been proposed in order to interpret this behaviour. A macroscale irradiation of 1-hydroxy-2-phenylindole affording several compounds has also been carried out.

1-Hydroxy-2-phenylindole **1** is the most representative and probably the most easily accessible among 1-hydroxyindoles, due to its easy preparation by cyclisation of α–benzoinoxime in sulphuric acid at room temperature.[1] In solution this compound exhibits tautomerism as shown in (1). As proved years ago, the ratio between en-



(1)

hydroxylamine (**1a**) and nitrone (**1b**) depends on the solvent.[2] Most of the work done on 1-hydroxy-2-phenylindole, like reactions with electrophilic reagents and oxidising agents,[3] was related to its enaminic form. The easy autoxidation of **1**[4] is justified by its low oxidation potential, which is 0.4 V *vs* $Ag/AgClO_4$.[5] Even though 1-hydroxy-2-phenylindole was first prepared at the end of the last century by Fisher,[1] no reaction of its nitronic form has been reported. This paper deals with nucleophilic attack of Grignard and alkyl lithium reagents on the latter form.

RESULTS AND DISCUSSION

Benzene solutions of 1-hydroxy-2-phenylindole were treated with Grignard **2a-c**, **2g-i** and alkyl lithium **3a**, **3d-f**, **3j** reagents at room temperature. The reaction mixture was extracted with benzene and then oxidised with activated lead dioxide.

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The ESR spectra corresponding to aminoxyls **5a-b, 5d, 5f, 5h-j** were recorded in chloroform and the hyperfine coupling constants (h.f.c.cs) are reported in Table 1. Aminoxyls **5** were detected in the reaction medium and no isolation of the solid compounds was possible: therefore no proof exists of attack by bulky groups **c, e, g**.

SCHEME 1

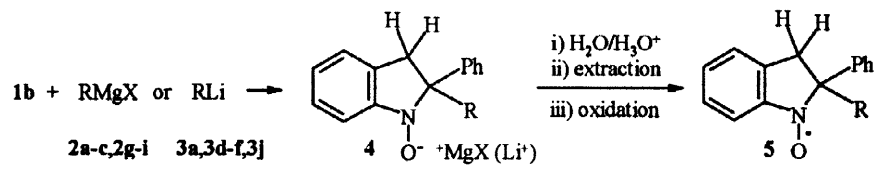
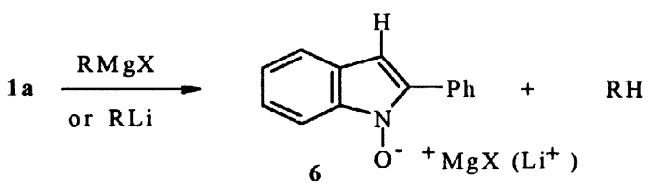


Table 1. Hyperfine coupling constants in gauss of aminoxyls **5a-b, 5d, 5f, 5h-j** recorded for $CHCl_3$ solutions.

Compound	a_N	$a_{H-3,7}$	$a_{H-4,6}$	a_{H-3}	a_{H-R}
5a	10.70(1N)	3.35(1H)	0.89(1H)	3.55(1H)	0.22(3H)
		3.19(1H)	1.06(1H)	2.66(1H)	
5b	10.62(1N)	3.41(1H)	0.86(1H)	3.39(1H)	0.27(1H)
		3.41(1H)	1.08(1H)	2.62(1H)	
5d	10.58(1N)	3.32(1H)	0.77(1H)	3.49(1H)	0.24(1H)
		3.31(1H)	1.14(1H)	2.50(1H)	
5f	10.62(1N)	3.25(1H)	0.98(1H)	3.58(1H)	0.17(1H)
		3.26(1H)	1.00(1H)	2.61(1H)	
5h	10.59(1N)	3.34(1H)	0.79(1H)	3.50(1H)	0.31(1H)
		3.19(1H)	1.26(1H)	2.61(1H)	
5i	10.66(1N)	3.37(1H)	0.62(1H)	3.48(1H)	0.22(1H)
		3.36(1H)	1.00(1H)	2.59(1H)	
5j	10.71(1N)	3.45(1H)	0.94(1H)	2.70(1H)	-
		3.26(1H)	0.97(1H)		

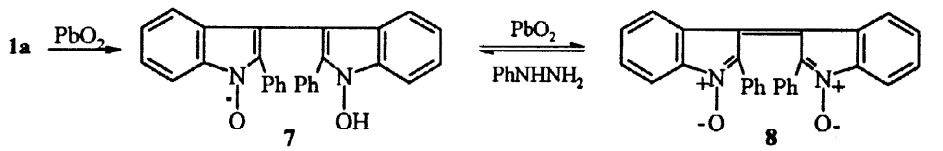


(2)

The same radical **5a** has been obtained both with Grignard and alkyl lithium, as shown by the same ESR spectrum (Table 1); reactions carried out with the more reactive alkyl lithium gave aminoxyls **5** in higher yields, as estimated from the more intense ESR signals. The ESR h.f.c.cs of aminoxyls **5** are consistent with the assigned structures and with the literature reports for similar compounds.[6] It is noteworthy that all aminoxyls, except for the 2,2-diphenyl substituted **5j**, show different ESR h.f.c.cs for the hydrogens at C-3: the presence of a stereogenic center at C-2 makes diastereotopic the two hydrogens at C-3 and their h.f.c.cs differ by about 1 gauss. A second observation from the data in Table 1 concerns the coupling constants of the α-hydrogens of the alkyl groups substituted at C-2: aminoxyl **5a** shows three hydrogens equally coupled with h.f.c.c. equal to 0.22 gauss, while **5b, 5d, 5h-i**, bearing a CH_2 at C-2, show only one of the two hydrogens, with h.f.c.cs in the range 0.22-0.27 gauss. The different magnetic behaviour of the two hydrogens may be attributed to the fact that $-CH_2R$ is bonded to a chiral C-2: the same behaviour was previously observed for

indolinonic aminoxyls.[7]

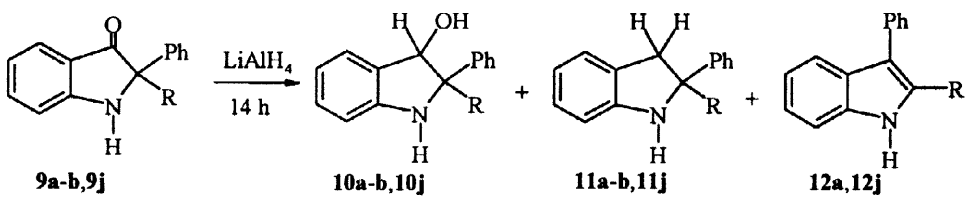
Treatment of 1-hydroxy-2-phenylindole with Grignard and alkyl lithium reagents did not afford complete transformation into aminoxyls **5**; on the contrary, most of **1a** was transformed (eq. 2) into the salt **6**, which regenerates **1** during hydrolysis in the working up of the reaction. Thus, hydrolysis of the reaction mixture gave a solution containing **1** and the hydroxylamino derivatives corresponding to anions **4**. By oxidation with lead dioxide, the latter were converted into aminoxyls **5**, while **1a** gave rise to the bis-nitrone **8**, through the "semiquinone" **7**, as shown in (3). Aminoxyls **5**, when formed, show much more intense ESR spectra than **7**, which, in spite of its formation, remains undetectable. On the contrary, only the ESR spectrum of **7** is detected when aminoxyls **5** did not form (**3c**, **3e**, **3g**). This spectrum consists of a triplet of triplets [a_N = 6.03 (1 N); $a_{H-5,7}$ = 1.53 (2 H) gauss, in benzene] and decreases in time: it corresponds to the one obtained by reduction of bis-nitrone **8** with a half equivalent of phenylhydrazine.



(3)

In order to demonstrate the structure of aminoxyls **5**, different synthesis of their precursors **11** were tried: (a) the reductive cyclization of 1-phenyl-1-alkyl-2-(*o*-nitrophenyl)ethanol with iron in acetic acid,

SCHEME 2



a: R=Me ; **b**: R=Et ; **j**: R=Ph

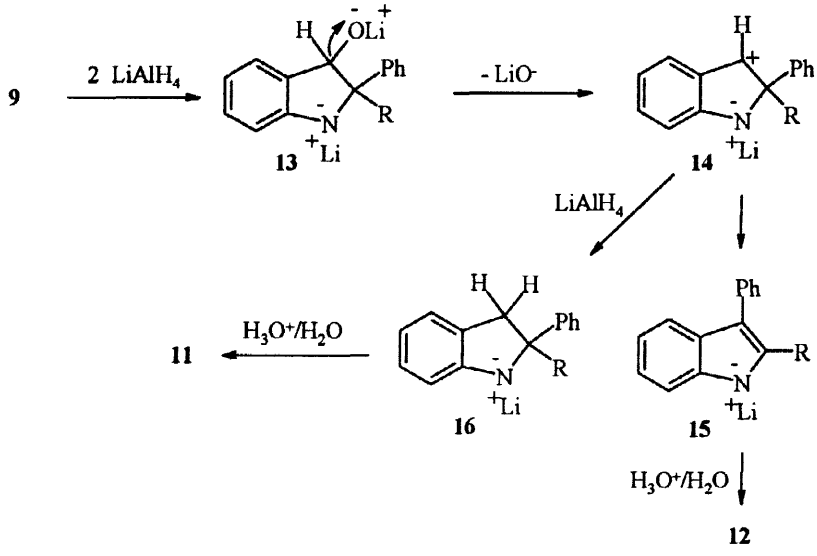
according to the method proposed for the reductive cyclization of *o*-nitrobenzylketones,[8] was not available, owing to the failure in obtaining the starting material; (b) treatment with potassium hydroxide of *o*-methylphenylimino acetophenone at 200 °C following the method described in the literature,[9] did not yield amine **11**; an attempt (c) to reduce the ketone group of compounds **9** in hot $P(OPr^i)_3$, according to the method described by Olah,[10] also failed. Compounds **11** were instead obtained by reduction of indoxyls **9** with $LiAlH_4$ in refluxing THF: the reduction lead to a mixture of

Table 2. Yields of compound **10a-b**, **10j**, **11a-b**, **11j**, **12a** and **12j** from $LiAlH_4$ reduction of **9a-b** and **9j**.

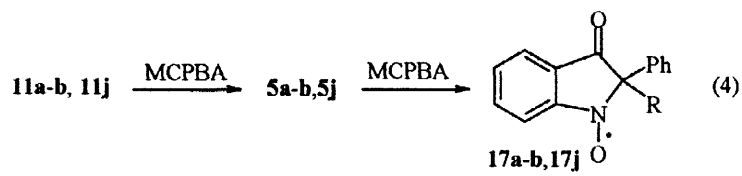
Reagent	Products (Yields %)		
9a	**10a** (60)[12]	**11a** (10)	**12a** (5)[13]
9b	**10b** (18)[12]	**11b** (70)	
9j	**10j** (63)[12]	**11j** (12)	**12j** (5)[13]

10, 11 and **12** (Scheme 2), whose yields are reported in Table 2; an attempt to transform **10** into **11** throughout the corresponding thionoformate followed by treatment with Bu^n_3SnH and AIBN was unsuccessful. [11] Finally, it was also ascertained that Clemmensen and Wolf - Kishner reductions of **9** did not yield the desired products. Compounds **10a-b, 10j**[12] and **12a, 12j**[13] were identified by comparison with authentic samples: **11a-b, 11j** by their spectroscopic data, which are in agreement with the structures assigned. The finding that oxidation with *m*-chloroperoxybenzoic acid (MCPBA) gave rise to the corresponding aminoxyls **5**, also confirms reciprocally the structures of compounds **5** and **11**. In particular, **11j** was isolated as stable crystals, whereas compounds **11a-b** were obtained as oils which tend to undergo spontaneous autoxidation if not protected under argon at low temperature. Indolines **11a-b** show different chemical shifts in their ^1H NMR spectra for the two hydrogens at C-3 (2.85 and 3.02 p.p.m., with a geminal coupling constant of 15.3 Hz, for **11a** ; 2.87 and 3.02 p.p.m., with a geminal constant of 15.4 Hz, for **11b**). These data agree with the different ESR h.f.c.cs of the two hydrogens at C-3 observed in aminoxyls **5a-b**.

SCHEME 3



The obtaining of compounds **11a-b, 11j** and **12a, 12j** by $LiAlH_4$ reduction of indoxyls **9a-b, 9j** asks for additional discussion (Scheme 3); since the reduction of the ketone group to the corresponding alcohol is a very well known process, it is without doubt that the reduction of **9** by $LiAlH_4$ leads to the intermediate **13** which is able to afford compounds **10** during hydrolysis. On the other hand intermediate **13** may lose the LiO^- anion forming the corresponding carbocation **14**, which may be reduced to **16**, which in turn is hydrolysed to indoline **11**[14]. Carbocation **14** may also undergo phenyl transposition leading to **15** from which indole **12** is formed; the higher migration power of the phenyl with respect to the alkyl group is well documented.[14] The oxidation of indolines **11a-b, 11j** with an excess of *m*-chloroperoxybenzoic acid (4) within the ESR cavity gave signals



(4)

corresponding to aminoxyls **5a-b, 5j** (Figure 1); the signals of **5** are changed with time and new signals grew in. In all cases the new signals correspond to those of aminoxyls **17a-b, 17j**.

Table 3. Hyperfine coupling constants (in gauss) of aminoxyls **19**, **28** and **30** in benzene.

Compound	a_N	$a_{H-5,7}$	$a_{H-4,6}$	a_{H-3}
19	9.37(1N)	3.16(1H) 3.33(1H)	0.92(1H) 0.96(1H)	0.10(1H) 1.54(1H)
28	9.45(1N)	3.18(1H) 3.35(1H)	0.92(1H) 0.98(1H)	1.58(1H)
30	9.22(1N)	2.91(1H) 3.08(1H)	0.96(1H) 1.04(1H)	-

Recently, it has been demonstrated that α-phenyl-*t*-butylnitrone (PBN), when irradiated by ultraviolet light in the presence of nucleophiles, leads to the formation of spin adducts.[15] Since 1-hydroxy-2-phenylindole **1a** behaves as a very good nucleophile, we irradiated a solution of the isomeric mixture **1** in the same conditions used for PBN with nucleophiles.[15] Irradiation of a benzene solution within the ESR cavity lead to detection of the signal reported in Figure 2a, to which the structure of the spin adduct **19** was tentatively assigned (Scheme 4). As a matter of fact the h.f.c.cs (Table 3), with two different values for the two hydrogens at C-3, seems to be in agreement with this structure.

In order to gain more detail on the formation of **19**, the irradiation was repeated in dioxane for 6 h. Working up the reaction, the products shown in Scheme 5 were isolated and identified by comparison with authentic samples; yields are reported in Table 4. Taking into account the results reported on PBN and those obtained in this experiment, indications in favour of the spin adduct **19** and of the products

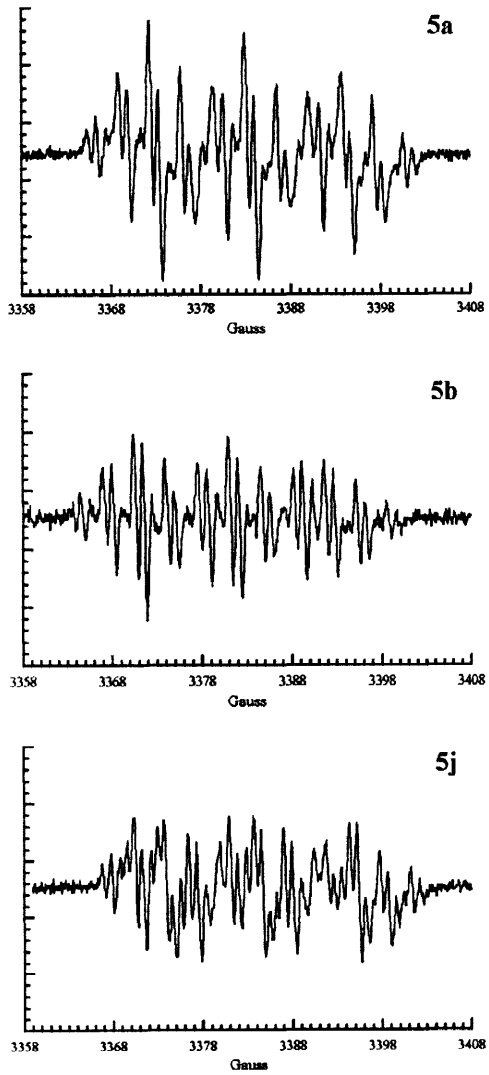
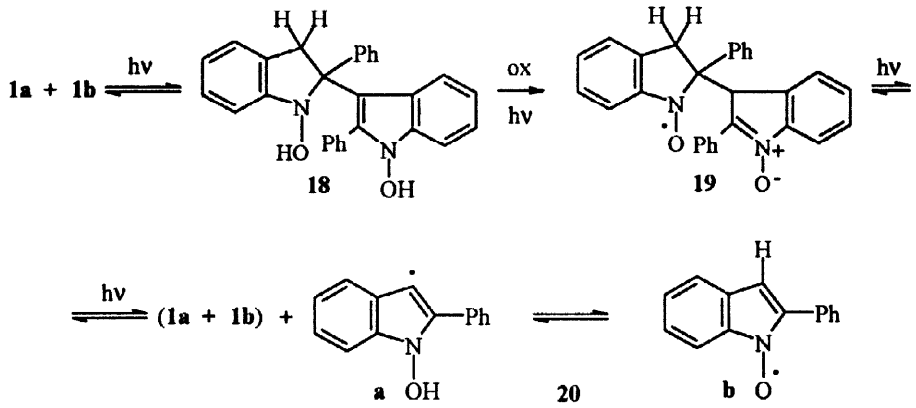


Fig. 1. ESR spectra of aminoxyls **5a**, **5b**, and **5j** in $CHCl_3$.

Table 4. Yields of compounds **8** , **21-25** for a conversion of 60% of **1.**

Compound	% Yields
8	8
21	22
22	25
23	16
24	1
25	1

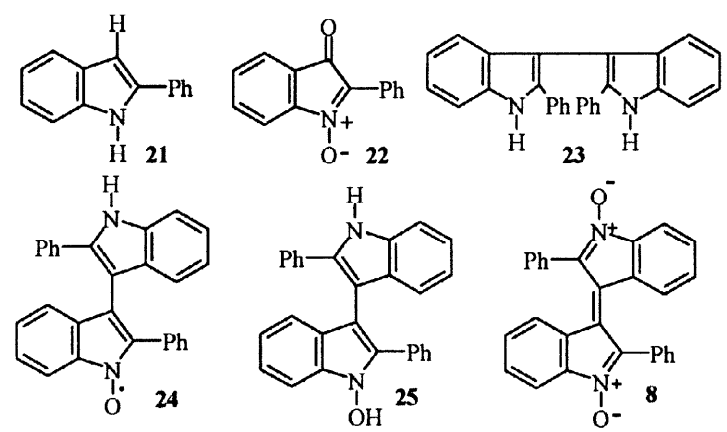
SCHEME 4

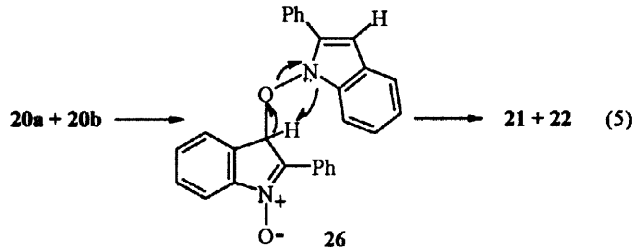


isolated and reported in Scheme 5, can be deduced. The formation of the spin adduct **19** may be explained on the basis of the Forrester-Hepburn nucleophilic addition of **1a** to its nitronic form **1b**, which gives **18**, and of the subsequent oxidation[16] of the latter (Scheme 4). The oxidation of the adduct **18** to the spin adduct **19** could be promoted by some weak acceptor under irradiation.[17] 2-Phenylindole **21** and 2-phenylisatogen **22** must be considered as the key products of the transformation of **1** under irradiation. In fact, these two compounds are the products of the disproportionation of indolyl radical **20**, which could likely be formed from homolytic scission of **19** during irradiation, as shown in Scheme 4. The one shown in (5) is the well known mechanism proposed for the disproportionation of nitroxides[18] and could explain the formation of compounds **21** and **22**. Bis-indoles **23-25** may be explained as arising from dimerization of the indolyl radical **20a** followed by partial or total deoxygenation, which can occur through a mechanism similar to that shown for the formation of 2-phenylindole **21** (5). The bis-nitrone **8** may probably arise from dimerization of **20a** followed by oxidation during the reaction work up.

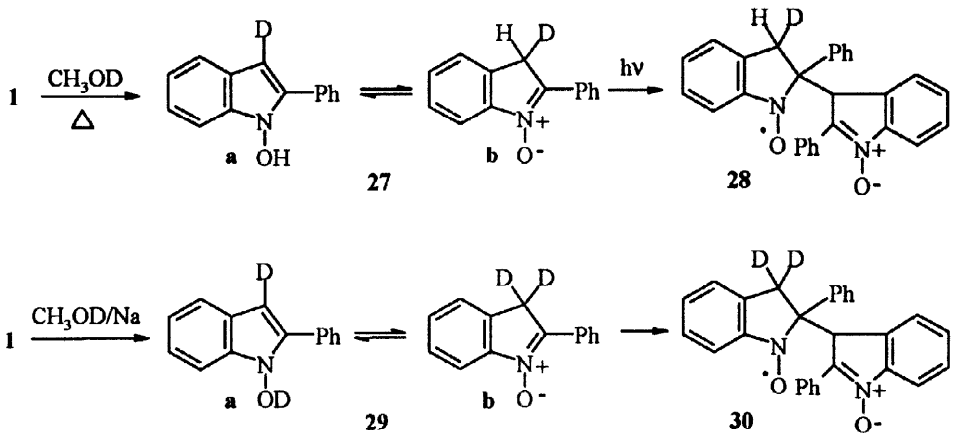
Additional experimental evidence supporting the equilibrium **1a** $\rightleftharpoons$ **1b** arises from the use of partially and totally deuterated 1-hydroxy-2-phenylindole. By refluxing the latter in CH_3OD, compound **27** was obtained (Scheme 6) while, if the same reaction is carried out in the presence of methoxylate anion, **30** is directly formed through **29** as shown by its ESR spectrum (Figure 2c); **27** was characterised by its NMR and mass spectrum (see experimental). Irradiation of **27** in benzene solution gave an ESR spectrum, which agrees with aminoxyl **28** (Figure 2b). The h.f.c.cs of aminoxyls **19** and **28** (Table 3) are quite similar, even though the corresponding ESR signals are rather different (Figures 2a and 2b). Since the

SCHEME 5





SCHEME 6



coupling constant of one of the two hydrogens (compound **19**) and the hydrogen (compound **28**) at C-3 are identical, the main difference is due to the fact that in **19** the smallest coupling at C-3 is 0.1 gauss for the second hydrogen and in **28** the coupling constant of deuterium, which is 1/10 with respect to that of the hydrogen, becomes negligible.

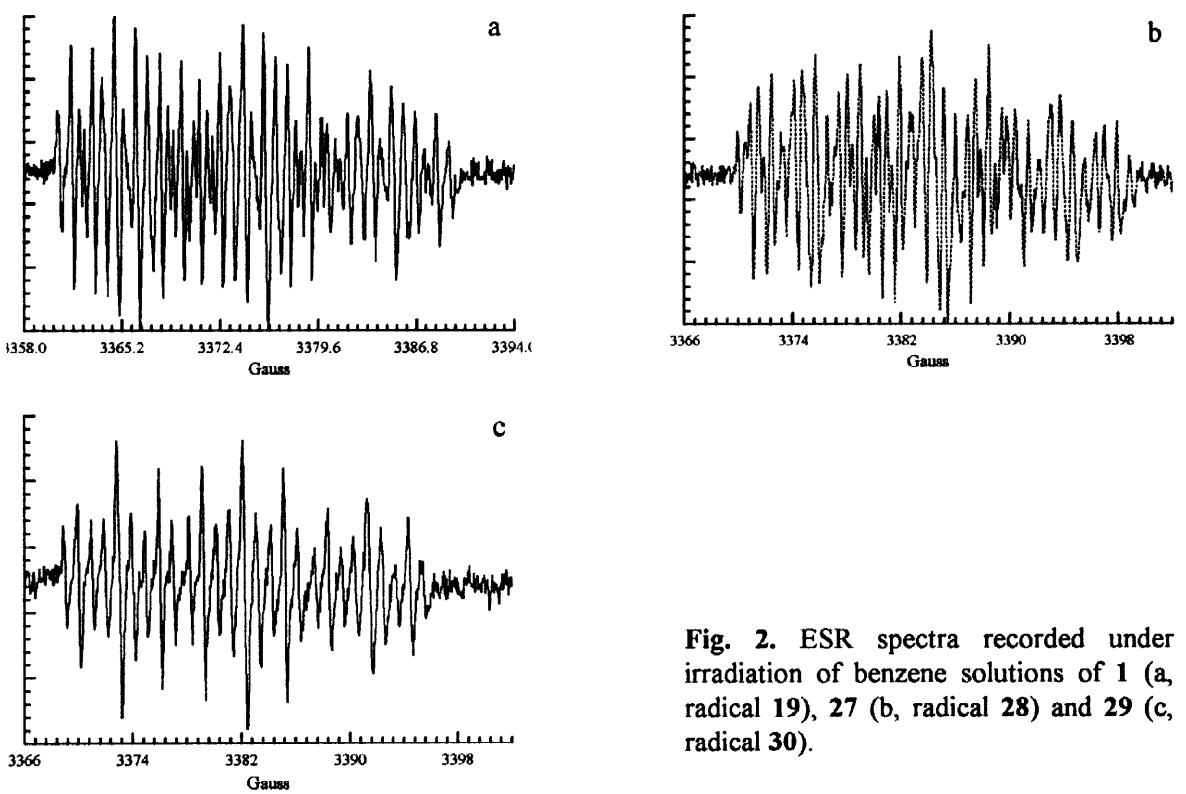


Fig. 2. ESR spectra recorded under irradiation of benzene solutions of **1** (a, radical **19**), **27** (b, radical **28**) and **29** (c, radical **30**).

The lack of any apparent coupling constant for the two deuteriums at C-3 and the previous considerations on **19** and **28** facilitates the interpretation of the ESR spectrum of **30** (Figure 2c).

EXPERIMENTAL

Melting points were uncorrected and were measured with an electrothermal apparatus. IR solid state spectra were measured on a Nicolet Fourier Transform Infrared 20-SX spectrophotometer equipped with a Spectra Tech. "Collector" for DRIFT measurements. ^{1}H NMR spectra were recorded at room temperature in $CDCl_3$ or C_6D_6 solution on a Varian Gemini 200 spectrometer (TMS was taken as reference peak). Mass spectra were taken with a Carlo Erba QMD 1000 mass spectrometer, equipped with a Fisons GC 8060 gaschromatograph. ESR spectra were recorded on a Varian E4 spectrometer interfaced with a computer (for acquisition, editing and simulation of experimental signals) and equipped with an XL microwave 3120 frequency counter and with a ruby in the cavity as reference.

1-Hydroxy-2-phenylindole **1**,[1] bis-nitrone **8**,[3f] 2,3-dihydro-2-phenyl-2-alkyl-3-oxoindole **9a-b and 9j**,[19] 2-phenylisatogen **22**,[20] 2-phenyl-3-(2-phenylindol-3-yl)indole **23**,[21] 1-oxyl-2-phenyl-3-(2-phenylindol-3-yl)indole **24**,[22] 1-hydroxy-2-phenyl-3-(2-phenylindol-3-yl)indole **25**[22] and lead dioxide[23] were synthesised according to the literature. Grignard and alkyl lithium reagents, lithium aluminium hydride, 3-chloroperoxybenzoic acid and 2-phenylindole **21** were purchased from Aldrich. All solvents were Carlo Erba or Aldrich RP-ACS grade and were purified according to the literature.[24]

Reaction of 1-hydroxy-2-phenylindole (1) with Grignard reagents (2a-c and 2g-i). General procedure. The Grignard reagent (1.5 mmol) was added dropwise, at room temperature, in a stream of argon to a solution of **1** (0.5 mmol) in anhydrous benzene (90 ml). The mixture was stirred for 1 h, then poured into aqueous 5% NH_4Cl and extracted with $CHCl_3$. The $CHCl_3$ layer was dried with Na_2SO_4 and evaporated to dryness; the residue was dissolved in $CHCl_3$ and filtered; the filtrate was treated with activated PbO_2 (10 mmol) for 1 h. ESR spectra of aminoxyls **5a-b** and **5h-i** were registered directly on the filtered solution (h.f.c.cs were reported in Table 1). In the case of **2c** and **2g** an ESR signal corresponding to **7** was recorded.

Reaction of 1-hydroxy-2-phenylindole (1) with alkyl lithium reagents (3a, 3d-f and 3j). General procedure. The alkyl lithium reagent (1.5 mmol) was added dropwise, at room temperature, in a stream of argon to a solution of **1** (0.5 mmol) in anhydrous benzene (90 ml). The mixture was stirred for 1 h, then poured into aqueous 5% NH_4Cl and extracted with $CHCl_3$. The $CHCl_3$ layer was dried with Na_2SO_4 and evaporated to dryness; the residue was dissolved in $CHCl_3$ and filtered; the filtrate was treated with activated PbO_2 (10 mmol) for 1 h. ESR spectra of aminoxyls **5a**, **5d**, **5f** and **5j** were registered directly on the filtered solution (h.f.c.cs were reported in Table 1). In the case of **3e** an ESR signal corresponding to **7** was registered.

Synthesis of 1-oxyl-2-phenyl-3-(1-hydroxy-2-phenylindol-3-yl)indole (7). Activated PbO_2 (50 mmol) was added at room temperature to a solution of 1-hydroxy-2-phenylindole, **1** (5 mmol) in $CHCl_3$ (100 ml). The mixture was stirred for 2 h, then filtered. This solution gave no ESR spectrum, because it contained only **8**. To the same solution, traces of phenylhydrazine were added. The ESR spectrum of the resulting solution is superimposable to that obtained during the previous reactions and is in agreement with structure **7**.

Reduction of 2,3-dihydro-2-phenyl-2-alkyl-3-oxoindole (9a-b,9j) with lithium aluminium hydride. General procedure. A solution of $LiAlH_4$ (53 mmol) in THF (30 ml) was added dropwise to a refluxing solution of **9** (5,3 mmol) in THF (20 ml). The mixture was stirred under reflux for 14 h, then poured into aqueous 5% NH_4Cl and extracted with diethyl ether. The organic layer was dried with Na_2SO_4 and evaporated to dryness; the residue was chromatographed on a SiO_2 column using cyclohexane as eluant, to which ethyl acetate was progressively added until a 9/1 ratio was obtained. Products were eluted in the order **11, 12** and **10** . The yields of the products are set out in Table 2, while the spectroscopic data of the new isolated compounds are reported below.

2,3-Dihydro-2-phenyl-2-methylindole (**11a**). M.p.: uncrystallizable material; IR (DRIFT) ν_{NH} 3363 cm^{-1}; ^{1}H-NMR (200 MHz, C_6D_6) δ 1.30 (3H, s, -CH_3), 2.85 (1H, d, -CH_2, J=15.3 Hz), 3.02 (1H, d, -CH_2, J=15.3 Hz), 3.29 (1H, s-br, -NH), 6.53 (1H,

dd, arom, J=7.7, J=0.9 Hz), 6.78(1H, td, arom, J=7.4, J=0.9 Hz), 6.97 (1H, d, arom, J=7.4 Hz), 7.15 (4H, m, arom), 7.33 (2H, m, arom); MS (EI^+) *m/z* 209 (M+, 70), 194 (100), 165 (51), 132 (52), 77 (48).

2,3-Dihydro-2-phenyl-2-ethylindole (**11b**). M.p.: uncrystallizable material; IR (DRIFT) ν_{NH} 3376 cm^{-1}; ^{1}H-NMR (200 MHz, C_6D_6) δ 0.56 (3H, t, $-CH_3$, J=7.3 Hz), 1.65 (1H, dq, $-CH_2-CH_3$, J=11.0, J=7.3 Hz), 1.72 (1H, dq, $-CH_2-CH_3$, J=11.0, J=7.3 Hz), 2.94 (1H, d, $-CH_2-$, J=15.4 Hz), 3.04 (1H, d, $-CH_2-$, J=15.4 Hz), 3.50 (1H, s-br, -NH), 6.56 (1H, d, arom, J=7.8 Hz), 6.77 (1H, td, arom, J=7.4, J=1.0 Hz), 6.96 (1H, d, arom, J=7.4 Hz), 7.26 (6H, m, arom); MS (EI^+) *m/z* 223 (M+, 45), 194 (100), 165 (47), 77 (30).

2,3-Dihydro-2,2-diphenyl indole (**11j**). M.p.: 124-5 °C; IR (DRIFT) ν_{NH} 3361 cm^{-1}; ^{1}H-NMR (200 MHz, $CDCl_3$) δ 3.47 (2H, s, $-CH_2-$), 3.83 (1H, s-br, -NH), 6.42 (1H, d, arom, J=7.5 Hz), 6.77 (1H, td, arom, J=7.5, J=0.9 Hz), 7.05 (8H, m, arom), 7.26 (4H, m, arom); MS (EI^+) *m/z* 271 (M+, 80), 194 (100), 165 (48), 77 (20).

*Oxidation of indolines (**11a-b,11j**) to aminoxyls (**5a-b,5j**) and (**17a-b,17j**). General procedure.* Solid 3-chloroperoxybenzoic acid (0.1 mmol) was added to a solution of **11** (0.01 mmol) in 1 ml of $CHCl_3$. The mixture was stirred for 2 min, then deaerated with argon for 2 min. ESR spectra of aminoxyls **5** were recorded. The signals corresponding to **5** changed in time until those of **17** appeared.

Irradiation of 1-hydroxy-2-phenylindole (1) into ESR cavity. Compound **1** (0.0047 mmol) was dissolved in benzene (1 ml) and the solution deaerated with Argon for 2 min in a quartz window cell. Irradiation was produced with a 250 W Hg lamp for 2 min, then ESR spectrum was recorded (Figure 2a).

Macroscale irradiation of 1-hydroxy-2-phenylindole (1). Compound **1** (14.7 mmol) was dissolved in dioxane (70 ml) in a photolizer and the solution irradiated with a 400 W Hg lamp for 6 h. The volume was reduced under vacuum, then diluted with 200 ml of water and extracted with $CHCl_3$ (3x40 ml). The organic layer was washed with water, dried with Na_2SO_4 and evaporated to dryness; the residue was chromatographed on a SiO_2 column using chloroform as eluant. The products, whose yields are set out in Table 4, were identified by comparison with authentic samples.[21]

Synthesis of 1-hydroxy-2-phenyl-3-D-indole (27). Solid 1-hydroxy-2-phenylindole **1** (0.048 mmol) was dissolved in CH_3OD (2 ml) and refluxed under stirring for 30 min. The solution was evaporated to dryness, treated with benzene (4 ml) and filtered. The conversion of **1** into **27** was complete: ^{1}H-NMR (200 MHz, $CDCl_3$) δ 7.06 (2H, m, arom), 7.43 (4H, m, arom), 7.70 (2H, m, arom), 8.40 (1H, m, arom), 8.95 (1H, s-br, -OH); MS (EI^+) *m/z* 210 (M+, 5), 193 (100), 165 (40), 77 (11).

Synthesis of 1-hydroxy-2-phenyl-1,3-DD-indole (29). Solid 1-hydroxy-2-phenylindole **1** (0.048 mmol) was added to a solution obtained dissolving Na (0.096 mmol) in CH_3OD (2 ml), under a stream of Argon and in absence of light. The solution was stirred for 5 min and then evaporated to dryness. The residue was taken up with benzene (4 ml) and filtered. Compound **29**, which undergoes in solution a rapid transformation to **30**, was identified by the ESR spectrum of the latter (Figure 2c).

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