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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. © 1998 Elsevier Science Ltd. All rights reserved.

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-

hydroxylamine (1a) and nitrone (1b) depends on the solvent.² Most of the work done on 1-hydroxy-2phenylindole, 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/AgClO₄.⁵ 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.

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.



Table 1. Hyperfine coupling constants in gauss of aminoxyls 5a-b, 5d, 5f, 5h-j recorded for CHCl₃ solutions.

Compound	an	8H-3.7	8 _{114,6}	a _{ii} .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)		

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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 CH₂ 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

(2) -CH₂R 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 bisnitrone 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 $[a_N = 6.03 (1 \text{ N}); a_{H}, 5.7 = 1.53 (2 \text{ H})$ 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.

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,



Table 2. Yields of compound 10a-b, 10j, 11ab, 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	11 b (7 0)			
9j	10j (63) ¹²	11j (12)	12j (5) ¹³		

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 $P(OPr')_3$, according to the method described by Olah,¹⁰ also failed. Compounds 11 were

instead obtained by reduction of indoxyls 9 with LiAlH₄ in refluxing THF: the reduction lead to a mixture of

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 Buⁿ₃SnH 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, 10j¹² and 12a, 12j¹³ 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.



The obtaining of compounds 11a-b, 11j and 12a, 12j by LiAlH₄ 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 LiAlH₄ 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



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.

Compound	8.N	84.57	a	8.0.2
		11-5,7	11-4.0	11-5
19	9.37(1N)	3.16(1H)	0.92(1H)	0.10(1H)
		3.33(1H)	0.96(1H)	1.54(1H)
28	9.45(1N)	3.18(1H)	0.92(1H)	1.58(1H)
		3.35(1H)	0.98(1H)	. ,
30	9.22(1N)	2.91(1H)	0.96(1H)	-
		3.08(1H)	1.04(1H)	

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

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



Fig. 1. ESR spectra of aminoxyls 5a, 5b, and 5j in CHCl₃.

(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

Table4.Yieldsofcompounds8, 21-25for aconversion of 60% of 1.

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



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 oxidation¹⁶ 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 nitroxides¹⁸ 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 = 1b arises from the use of partially



and totally deuterated 1-hydroxy-2phenylindole. By refluxing the latter in CH₃OD, 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









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.



3382

Gaus

3374

3366

3390



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).

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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. ¹H NMR spectra were recorded at room temperature in CDCl₃ 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 8,³⁷ 2,3-dihydro-2-phenyl-2-alkyl-3-oxoindole 9a-b and 9j.¹⁹ 2-phenylisatogen 22,²⁰ 2-phenyl-3-(2-phenyl-3-(2-phenyl-3-(2-phenylindol-3-yl))indole 25,²¹ 1-oxyl-2-phenyl-3-(2-phenylindol-3-yl)indole 25,²² and lead dioxide²³ 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% NH₄Cl and extracted with CHCl₃. The CHCl₃ layer was dried with Na₂SO₄ and evaporated to dryness: the residue was dissolved in CHCl₃ and filtered; the filtrate was treated with activated PbO₂ (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% NH₄Cl and extracted with CHCl₃. The CHCl₃ layer was dried with Na₂SO₄ and evaporated to dryness; the residue was dissolved in CHCl₃ and filtered; the filtrate was treated with activated PbO₂ (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 PbO₂ (50 mmol) was added at room temperature to a solution of 1-hydroxy-2-phenylindole, 1 (5 mmol) in CHCl₃ (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 LiAlH₄ (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% NH₄Cl and extracted with diethyl ether. The organic layer was dried with Na₂SO₄ and evaporated to dryness; the residue was chromatographed on a SiO₂ 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) $v_{\rm MI}$ 3363 cm⁻¹; ¹H-NMR (200 MHz, C₆D₆) δ 1.30 (3H, s, -CH₃), 2.85 (1H, d, -CH₂, J=15.3 Hz), 3.02 (1H, d, -CH₃, 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) v_{NH} 3376 cm⁻¹; ¹H-NMR (200 MHz, C₆D₆) δ 0.56 (3H, t, -CH₃, J=7.3 Hz), 1.65 (1H, dq, -CH₂-CH₃, J=11.0, J=7.3 Hz), 1.72 (1H, dq, -CH₂-CH₃, J=11.0, J=7.3 Hz), 2.94 (1H, d, -CH₂-, J=15.4 Hz), 3.04 (1H, d, -CH₂-, 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) v_{NH} 3361 cm⁻¹; ¹H-NMR (200 MHz, CDCl₃) δ 3.47 (2H, s, -CH₂-), 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 3chloroperoxybenzoic acid (0.1 mmol) was added to a solution of 11 (0.01 mmol) in 1 ml of CHCl₃. 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 CHCl₃ (3x40 ml). The organic layer was washed with water, dried with Na₂SO₄ and evaporated to dryness; the residue was chromatographed on a SiO₂ 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 CH₃OD (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: ¹H-NMR (200 MHz, CDCl₃) 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 CH₃OD (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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REFERENCES

- 1. Fisher, E. Chem. Ber. 1896, 29, 2062.
- a) Angeli, A.; Angelico, F. Atti Accad. Lincei, 1906, XV, 98. b) Mousseron-Canet, M.; Boca, J.P. Bull. Soc. Chim. Fr. 1967, 4, 1296-1302.
- a) Colonna, M.; Bruni, P. *Ric. Sci. Rend.* [2], 1964, A4, 151; *Chem. Abstr.* 1964, 61, 633. b) Colonna, M.; Bruni, P. Gazz. Chim. Ital. 1964, 94, 1448. c) Colonna, M.; Bruni, P. Gazz. Chim. Ital. 1965, 95, 1172. d) Colonna, M.; De Martino, U. Gazz. Chim. Ital. 1963, 93, 1183. e) Colonna, M.; Monti, A. Gazz. Chim. Ital. 1962, 92, 1401. f) Colonna, M.; Greci, L. Gazz. Chim. Ital. 1969, 99, 351.
- 4. Passalacqua, V.; Marchetti, L. Bull. Sci. Fac. Chim. Ind. Bologna 1969, 27, 119.
- 5. Andruzzi, R.; Berti, C.; Greci, L.; Trazza, A. J. Chem. Res. (S) 1983, 256.
- 6. Rozantsev, E.G. Free Nitroxyl Radicals; Plenum Press: New York, 1970; p. 139.
- 7. Colonna, M.; Greci, L.; Berti, C.; Marchetti, L. Tetrahedron 1975, 31, 1745.
- 8. a) Raissert, A. Chem. Ber. 1897, 30, 1030. b) Rosemund, P.; Haase, W.H. Chem. Ber. 1966, 99, 2504.
- 9 Preston, P.N.; Tennant, G. Chemical Reviews 1972, 72, 1972
- 10. Olah, G.A.; Wu, A. Synlett. 1990, 54.
- 11. Khazanchi, R.; Yu, P.L.; Johnson, F. J. Org. Chem. 1993, 58, 2552-6.
- 12. Berti, C.; Greci, L.; Poloni, M. J. Chem. Soc. Perkin Trans. 2 1980, 710.
- 13. Berti, C.; Greci, L.; Poloni, M. J. Chem. Soc. Perkin Trans. 1 1981, 1610.
- a) Sundberg, R.J. The Chemistry Of Indoles; Academic Press: London, 1970. b) Haulian, W.J. Indoles Part 1 in the Chemistry of Heterocyclic Compounds; Wiley-Interscience: New York, London, 1978.
- a) Carloni, P.; Eberson, L.; Greci, L.; Sgarabotto, P.; Stipa, P. J. Chem. Soc. Perkin Trans. 2 1996, 887. b) Eberson, L. J. Chem. Soc. Perkin Trans. 2 1994, 171.
- 16. Forrester, A.R.; Hepburn, S.P. J. Chem. Soc. 1971, 701.
- 17. In the discussion reported in : Eberson, L.; Lind, J.; Merenyi, G., J. Chem. Soc. Perkin Trans. 2 1994, 1181.
- 18. a) Greci, L. Tetrahedron 1982, 39, 677. b) Forrester, A.R.; Thomson, R.H. Nature 1964, 77, 203.
- a) Berti, C.; Greci, L.; Marchetti, L. J. Chem. Soc. Perkin Trans. 2 1977, 1032. b) Berti, C.; Greci, L.; Marchetti, L. J. Chem. Soc. Perkin Trans. 2 1979, 233.
- 20 Bond, C. C. Synthesis 1974, 443.
- 21 Colonna, M.; Monti, A. Gazz Chim Ital 1962,92, 14.
- 22 Colonna, M.; Greci, L., Marchetti, L. Gazz Chim Ital 1976,106, 197.
- 23 Kuln, R.; Hammer, I. Chem. Ber. 1950, 83, 413.
- 24 Vogel, A.J. A textbook of practical organic chemistry 4 th ed., Longmans: Essex, England, 1988.