to proceed with stirring at room temperature. Reaction times were of the order of 1–5 h, and the reaction was complete when all the inorganic salt had dissolved.

The reaction mixture was poured into 50 mL of water and extracted three times with 15-mL portions of chloroform. Products were isolated by trapping from GLC and characterized by comparing their infrared, NMR, and mass spectra with those from authentic samples of the compounds.

General Procedure for the Nitration of Benzene with Acids and Anhydrides Other Than TFA and TFAA. By the same procedure as described above, 5 mL of benzene was nitrated with 0.01 mol (0.80 g) of ammonium nitrate in 70 mL of $CHCl_3$. In these cases, TFAA was replaced by 0.35 mol of the appropriate acid or anhydride. Reactions were carried out at 25 °C for 2 h, and the products were analyzed by GLC.

General Procedure for the Nitration of Polymers. Into a 100-mL resin flask equipped with a reflux condenser, magnetic stirrer, and drying tube were placed 0.02 mol (based on segmer molecular weight) of the polymer, 0.02 mol of NH_4NO_3, 70 mL of chloroform, and 10 mL of TFAA. In most cases, the reaction mixture was stirred at room temperature for 15 h, although the salt had dissolved within 3 h. During this time, the polymer solution took on a yellow or orange color. The polymers were precipitated into either *n*-hexane or methanol, washed with water, and dried at 60 °C in vacuo.

General Procedure for the Oxidation of Phenols. To a 100-mL single-neck flask equipped with a magnetic stirrer, reflux condenser, and drying tube were placed 0.01 mol of the phenol, 0.02 mol of NH_4NO_3, 0.05 mol of TFAA, and 50 mL of the indicated solvent. Reaction occurred spontaneously, and the reaction temperature was controlled by placing the flask in a water bath at 25 °C. The reaction was complete within 2–5 h when the inorganic salt had dissolved. In all cases the product was insoluble in the medium and was recovered by filtration. After the quinone was washed with a small amount of the reaction solvent, it was dried for 15 h in a vacuum oven.

Oxidation of Pentachlorophenol. Into a 500-mL reaction vessel equipped with a stirrer, thermometer, reflux condenser, and drying tube were placed 26.6 g (0.01 mol) of pentachlorophenol, 8 g (0.1 mol) of NH_4NO_3, and 300 mL of methylene chloride. To this mixture was added 20 mL (0.13 mol) of TFAA, and the reaction mixture was stirred in a water bath for 4 h at 25–30 °C. The reaction mixture was filtered to remove impure tetrachloro-1,4-benzoquinone, and the solvent was removed from the filtrate by means of a rotary evaporator. The solid which remained was dissolved in hot cyclohexane, filtered, and allowed to crystallize to give 19.74 g (80% yield) of tetrachloro-1,2-benzoquinone, mp 122–126 °C (lit.[18] mp 121–127 °C). Anal. Calcd for $C_6Cl_4O_2$: C, 29.27; Cl, 57.24; O, 13.49. Found: C, 29.16; Cl, 57.55; O, 13.29. Further workup of the impure tetrachloro-1,4-benzoquinone gave an 8.5% yield of pure quinone, mp 290 °C (lit.[17] mp 290 °C).

Registry No. $(CF_3CO)_2O$, 407-25-0; $(CCl_3CO)_2O$, 4124-31-6; $(Cl_2CHCO)_2O$, 4124-30-5; CF_3COOH, 76-05-1; NH_4NO_3, 6484-52-2; $NaNO_3$, 7631-99-4; KNO_3, 7757-79-1; $Cu(NO_3)_2$, 3251-23-8; $AgNO_3$, 7761-88-8; $Pb(NO_3)_2$, 10099-74-8; $Cd(NO_3)_2$, 10325-94-7; $Cr(NO_3)_3$, 13548-38-4; $NaNO_2$, 7632-00-0; C_6H_6, 71-43-2; $C_6H_5CH_3$, 108-88-3; C_6H_5Cl, 108-90-7; C_6H_5COOH, 65-85-0; $C_6H_5NH_2$, 62-53-3; benzothiazole, 95-16-9; 1-phenyl-1*H*-pyrrole-2,5-dione, 941-69-5; $C_6H_5OCH_3$, 100-66-3; $C_6H_5OCH_2C{\equiv}CH$, 13610-02-1; C_5H_{10}, 91-20-3; C_6H_5-C_6H_5, 92-52-4; $C_6H_5OC_6H_5$, 101-84-8; $(C_6H_5)_3P$, 603-35-0; poly[oxycarbonyloxy-1,4-phenylene(1-methylethylidene)-1,4-phenylene], 24936-68-3; ethyenylbenzene homopolymer, 9003-53-6; poly[oxy-2,4-hexadiyne-1,6-diyloxy-1,4-phenylene(1-methylethylidene)-1,4-phenylene], 41227-07-0; poly(oxy[1,1′:3,1″-terphenyl]-2′,5′-diyl), 24938-68-9; 2,6-di-*tert*-butylphenol, 128-39-2; 2,6-dimethoxyphenol, 91-10-1; 2,6-dimethylphenol, 576-26-1; 2,6-diphenylphenol, 2432-11-3; tetrachlorohydroquinone, 87-87-6; pentachlorophenol, 87-86-5; $C_6H_5NO_2$, 98-95-3; *o*-$NO_2C_6H_4CH_3$, 88-72-2; *m*-$NO_2C_6H_4CH_3$, 99-08-1; *p*-$NO_2C_6H_4CH_3$, 99-99-0; *o*-$NO_2C_6H_4Cl$, 88-73-3; *p*-$NO_2C_6H_4Cl$, 100-00-5; *m*-$NO_2C_6H_4COOH$, 121-92-6; *o*-$NO_2C_6H_4NHC(O)CF_3$, 2727-72-2; 6-nitrobenzothiazole, 2942-06-5; 1-(2-nitrophenyl)-1*H*-pyrrole-2,5-dione, 52274-95-0; 1-(4-nitrophenyl)-1*H*-pyrrole-2,5-dione, 4338-06-1; *o*-$NO_2C_6H_4OCH_3$, 91-23-6; *p*-$NO_2C_6H_4OCH_3$, 100-17-4; *o*-$NO_2C_6H_4OCH_2C{\equiv}CH$, 13350-09-9; *p*-$NO_2C_6H_4OCH_2C{\equiv}CH$, 17061-85-7; 1-$NO_2C_{10}H_7$, 86-57-7; 2-$NO_2C_{10}H_7$, 581-89-5; *o*-$NO_2C_6H_4C_6H_5$, 86-00-0; *p*-$NO_2C_6H_4C_6H_5$, 92-93-3; *o*-$NO_2C_6H_4C_6H_4NO_2$-*o*, 2436-96-6; *o*-$NO_2C_6H_4C_6H_4NO_2$-*p*, 606-81-5; *p*-$NO_2C_6H_4C_6H_4NO_2$-*p*, 1528-74-1; *o*-$NO_2C_6H_4OC_6H_4NO_2$-*o*, 2217-65-4; *o*-$NO_2C_6H_4OC_6H_4NO_2$-*p*, 5950-83-4; *p*-$NO_2C_6H_4OC_6H_4NO_2$-*p*, 101-63-3; $(C_6H_5)_3PO$, 791-28-6; carbonic acid, polymer with 4,4′-(1-methylethylidene)bis[phenol], 25037-45-0; 3,3′,5,5′-tetra-*tert*-butyldiphenoquinone, 2455-14-3; 3,3′,5,5′-tetramethoxydiphenoquinone, 493-74-3; 3,3′,5,5′-tetramethyldiphenoquinone, 4906-22-3; 3,3′,5,5′-tetraphenyldiphenoquinone, 3550-01-4; 2,6-diphenyl-1,4-benzoquinone, 2887-97-0; tetrachloro-1,4-benzoquinone, 118-75-2; tetrachloro-1,2-benzoquinone, 2435-53-2.

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Nucleophilic Substitutions on 1,2-Dihydro-2,2-disubstituted-3-oxo-3*H*-indole-1-oxyl Radicals. Direct Acyloxylation and Methoxylation

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1,2-Dihydro-3-oxo-3*H*-indole-1-oxyl (1) undergoes direct acyloxylation and methoxylation on the indole ring when treated with lead(IV) in the presence of acyl anions or methanol. The reaction has been interpreted by assuming the intermediate formation of an oxoammonium salt.

On the basis of their structure, nitroxide radicals can be divided into two main groups:[1] (i) stable nitroxides, with the unpaired electron localized on the N-O· group, i.e., 2,2,6,6-tetramethylpiperidine-1-oxyl or 2,2,5,5-pyrrolidine-1-oxyl, and (ii) relatively stable nitroxides with the unpaired electron delocalized in the molecule through the conjugated π system, i.e., alkyl aryl or diaryl nitroxides. The well-studied chemical behavior of the two different groups (e.g., reduction to hydroxylamines,[2] oxidation to

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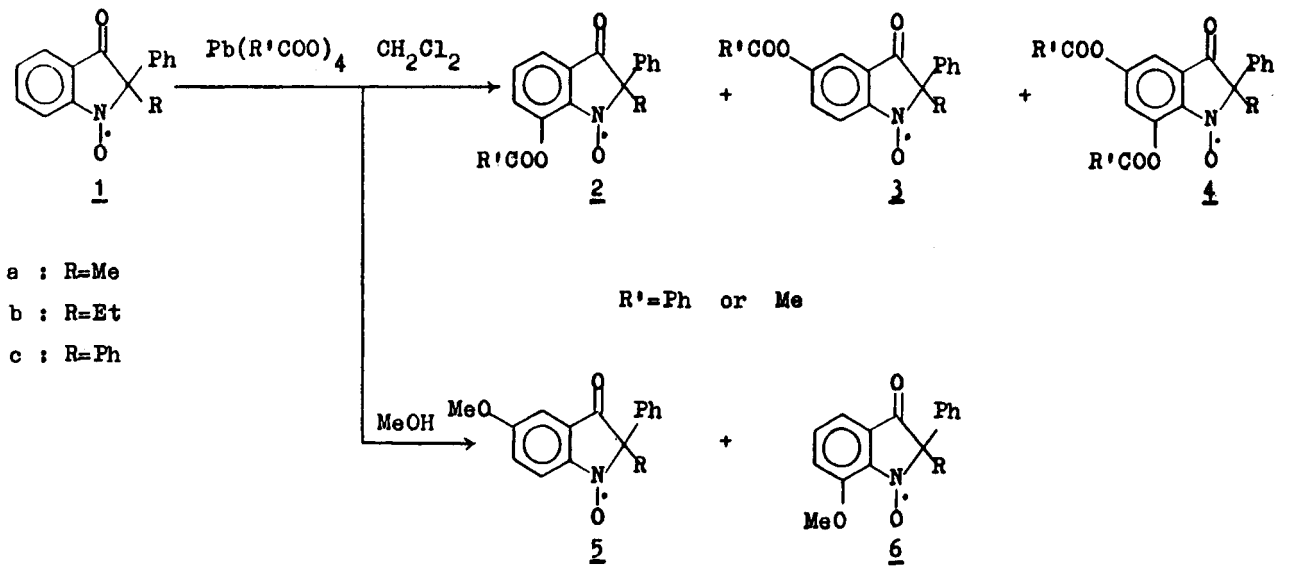
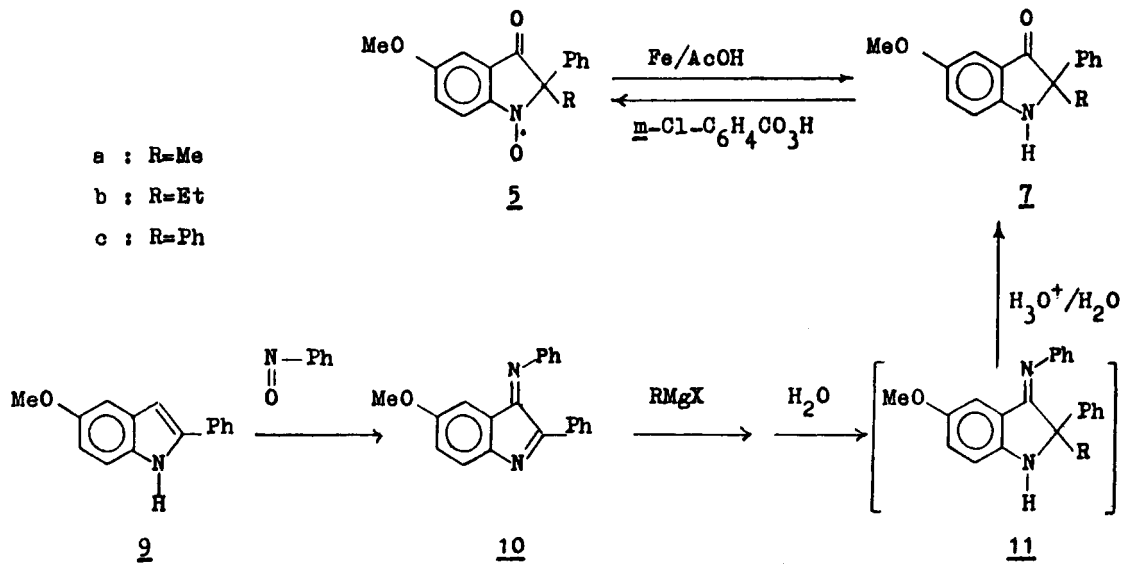
Scheme I



Scheme II



oxoammonium salts,[3] addition of hydrocarbon radical,[4] etc.), is quite similar and differs only in the disproportionation reaction,[5] which in solution is a spontaneous process for most nitroxides of the second group. Direct acyloxylation and methoxylation, described in this paper, confirms a new kind of reactivity of perfectly stable nitroxides 1,[6] in which the N-O· group is in the position conjugated with the π system of the molecule.

Results

Nitroxide radicals 1[6] react with lead tetrabenzoate or tetraacetate to form acyloxy derivatives 2–4 (Scheme I). Reactions were carried out in methylene chloride at room temperature by using the lead salt in 20% excess. Compounds 2–4 were isolated by SiO_2 preparative TLC and identified by their spectroscopic data. All compounds gave the expected molecular ion peak in their mass spectra. IR spectra showed three characteristic bands at 1600, 1730–1735, and 1740–1780 cm^{-1}, which correspond to $C_6H_5N(O)C$,[7] CO, and R'COO groups, respectively. In particular it was observed that the band at 1745–1780 cm^{-1} was more intense that the one at 1730–1735 cm^{-1} for the acyloxy disubstituted 4. Hfccs of the ESR spectra (Table I) were consistent with the assigned structures and were in agreement with those of other nitroxide radicals of this type previously described.[8,9] The structure of isomeric nitroxides 2 and 3 was established as we previously described.[8]

When the reaction between nitroxide radicals 1 and lead tetrabenzoate and tetraacetate was performed in methanol at room temperature, methoxy-substituted nitroxide radicals 5 and 6 were isolated as the main products together with a small amount of compounds 2 and 3 (Scheme I). Since the hfccs of nitroxides **5a–c** and **6a–c** (Table II) could not be compared with those of nitroxides 2 and 3, the structures of **5a–c** were determined by ^1H NMR study of the amines **7a** and **7c** obtained from nitroxides **5a** and

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Scheme III

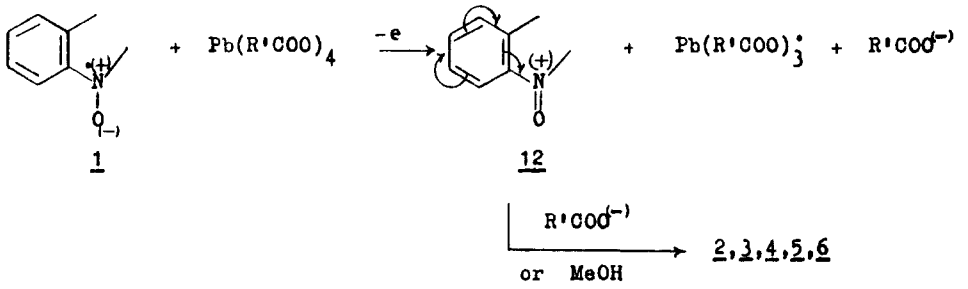
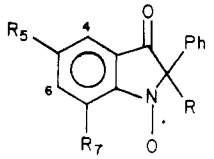


Table I. ESR hfccs[a] of Nitroxides 2-4 in $CHCl_3$ Solution

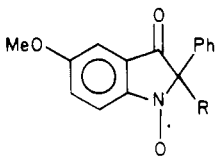


R	R_5	R_7	a^N	a^{H-5} (1 H)	a^{H-7} (1 H)	$a^{H-4} = a^{H-6}$ (2 H)	a^{HR}
Me	PhCOO	H	9.62		2.98	1.01	0.12 (3 H)
Et	PhCOO	H	9.45		2.95	1.02	0.28 (1 H)
Ph	PhCOO	H	9.50		2.85	1.00	
Me	MeCOO	H	9.56		2.95	1.01	0.10 (3 H)
Et	MeCOO	H	9.45		2.95	1.02	0.28 (1 H)
Ph	MeCOO	H	9.49		2.94	1.00	
Me	H	PhCOO	9.12	3.20		0.97	0.11 (3 H)
Et	H	PhCOO	9.07	3.18		0.98	0.30 (1 H)
Ph	H	PhCOO	9.19	3.21		0.98	
Me	H	MeCOO	9.30	3.15		0.99	0.15 (3 H)
Et	H	MeCOO	9.18	3.26		1.00	0.30 (1 H)
Ph	H	MeCOO	9.21	3.12		0.98	
Me	PhCOO	PhCOO	9.22			0.98	0.22 (3 H)
Et	PhCOO	PhCOO	9.17			1.00	0.30 (1 H)
Ph	PhCOO	PhCOO	9.20			0.97	
Me	MeCOO	MeCOO	9.30			1.00	0.14 (3 H)
Et	MeCOO	MeCOO	9.23			1.00	0.30 (1 H)
Ph	MeCOO	MeCOO	9.25			0.98	

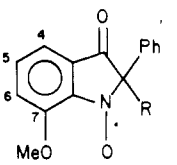
[a] These values were confirmed by experimental spectra simulation.

5c by iron–acetic acid reduction (Scheme II). ^1H NMR spectra of both **7a** and **7c** showed a doublet at δ 6.91 (J = 8.0 Hz) and a pseudoquartet at δ 7.09 (J = 8.0, 2.2 Hz) relative to the hydrogens at C-7 and C-6, respectively. This result confirmed that the methoxy group was linked to C-5, if we assume that only C-5 and C-7 was involved in the reaction, as will be explained later. The final confirmation of the structure of compounds **7a** and **7c** was obtained by an independent synthesis which followed the pathway: **9** → **10** → **11** → **7** (Scheme II). Unknown compounds **9**,[10] **10**,[11] and **11**[12] where synthesized according to the methods described in the literature.

Table II. ESR hfccs[a] of Nitroxides 5 and 6 in $CHCl_3$ Solution



5



6

	a^N	a^{H-7} or a^{H-5}	a^{H-4}; a^{H-6}	a^{HOMe}	a^{HR}
5a	9.95	2.72 (1 H)[b]	1.30 (1 H); 0.78 (1 H)	0.40 (3 H)	0.18 (3 H)
5b	9.80	2.70 (1 H)[b]	1.35 (1 H); 0.77 (1 H)	0.40 (3 H)	
5c	9.80	2.70 (1 H)[b]	1.28 (1 H); 0.80 (1 H)	0.40 (3 H)	
6a	9.95	3.50 (1 H)[c]	1.00 (1 H)	0.40 (3 H)	0.17 (3 H)
6b	9.90	3.50 (1 H)[c]	0.95 (1 H)	0.40 (3 H)	
6c	9.90	3.47 (1 H)[c]	0.90 (1 H)	0.42 (3 H)	

[a] These values were confirmed by experimental spectra simulation. [b] a^{H-7}. [c] a^{H-5}.

The amines **7a** and **7c** prepared in this way gave nitroxides **5a** and **5c**, respectively, by oxidation with *m*-chloroperbenzoic acid (Scheme II). The structure of nitroxides **6a–c**, which in solution were red (nitroxides **5a–c** were green), was established on the basis of the H-5 hfcc, which was greater than that of H-7 for nitroxides **5a–c** (Table II), in agreement with that previously described.[8]

Discussion

Direct acyloxylations have already been carried out on different substrates, i.e., anisole,[13] dimethylanilines,[14] and methylbenzenes.[15] These reactions were interpreted by hypothesizing the formation of a radical cation intermediate which undergoes nucleophilic attack.

However, the reactions described in our paper were interpreted by assuming the intermediate formation, through the monoelectronic oxidation of nitroxide **1**, of the oxoammonium salt **12**,[16] which would easily react with nucleophilic species (Scheme III).

In the methoxylation, the lower nucleophilicity of the methanol in comparison with that of the acyl anion, was

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(16) The electrochemical oxidation of nitroxides **1** involves only one electron and is reversible. This result indirectly confirms the formation of the oxoammonium compound **12** (C. Berti, L. Greci, R. Andruzzi, and A. Trazza, unpublished result).

compensated by the large amount of methanol used as the reaction solvent.

All attempts to isolate oxoammonium salts **12** failed because of their high reactivity at C-5 and C-7, which are the positions conjugated with the oxoammonium group. The acyloxylation and methoxylation described in this paper and the bromination previously described by one of us[9] can be considered to be a new nucleophilic substitution of nitroxide radicals having the N-O· function in the position conjugated with a π system.

Experimental Section

Melting points are uncorrected, ^{1}H NMR spectra were recorded in deuterated chloroform with a Varian XL-100 spectrometer with internal tetrmethylsilane as the reference. IR spectra were recorded on a Perkin-Elmer 257 spectrophotometer as Nujol mulls, unless otherwise specified. Mass spectra were recorded on a Varian 112 S spectrometer. ESR spectra were recorded on a Varian E4 for the chloroform solutions.

Reactions of Nitroxides 1a–c with Lead Tetraacetate and Lead Tetrabenzoate in CH_2Cl_2. Lead tetraacetate or tetrabenzoate (1.2 mmol) was added to a solution of **1a–c** (1 mmol in 30 mL of CH_2Cl_2) with stirring and at room temperature. After 24 h the mixture was filtered and the filtrate evaporated to dryness. The residue was taken up with benzene (50 mL). The benzene solution was washed with 10% aqueous $NaHCO_3$ (50 mL) and water (3 × 30 mL). The benzene layer, dried over Na_2SO_4, was chromatographed on a column of silica gel with ethyl acetate–petroleum ether as the eluent. Yields were 18–24%, 28–37%, and 2–6% for the isolated compounds **2–4** respectively. The substituted benzoyloxy compounds showed IR spectra with three bands at 1600, 1730, and 1745 cm^{-1}, whereas the corresponding acetyloxy compounds showed three bands at 1600, 1735, and 1780 cm^{-1}. All spectra were recorded in $CHCl_3$. Compounds **2–4** are solids. Owing to their low stability, it was impossible to have them in a state sufficiently pure for elemental analysis; nevertheless some of them have been previously analyzed.[8]

Reaction of Nitroxides 1a–c with Lead Tetraacetate and Lead Tetrabenzoate in MeOH. Lead tetrabenzoate or tetraacetate (2 mmol) was added to a solution of **1a–c** (1 mmol in 100 mL of MeOH) with stirring at room temperature. After 24 h the reaction was worked up as described above. Compounds **5** and **6** were isolated in 45–55% and 20–25% yields, respectively, together with traces of nitroxides **2** and **3**. Compounds **5** and **6** are solids but were not stable enough for analysis.

2-Phenyl-5-methoxyindole (9). This compound was prepared according to Fischer's method.[10] (*p*-Methoxyphenyl)hydrazine (0.1 mol), acetophenone (0.1 mol), and dried $ZnCl_2$ (20 g) were heated in a beaker at ca. 200 °C for 15 min. The product was poured into hot 10% HCl (100 mL), and the liberated indole was extracted with benzene (100 mL). The separated benzene layer, dried on Na_2SO_4, was chromatographed on a silica gel column eluting with benzene. Indole **9** was isolated in 70% yield: mp 170 °C (from ligroin, bp 100–135 °C); ^{1}H NMR ($CDCl_3$) δ 3.88 (s, 3 H, OCH_3), 6.7–7.7 (m, 10 H, aromatics). Anal. Calcd for $C_{15}H_{13}NO$: C, 80.69; H, 5.86; N, 6.27. Found: C, 80.72; H, 5.75; N, 6.32.

2-Phenyl-3-(phenylimino)-5-methoxy-3*H*-indole (10). 2-Phenyl-5-methoxyindole (**9**, 10 mmol) and nitrosobenzene (10 mmol) were heated in 40 mL of absolute ethanol. To this boiling solution was added 1 mL of 10% sodium ethylate dropwise. When the mixture cooled, the imino derivative **10** precipitated in the reaction solution: mp 157 °C (from ethanol); ^{1}H NMR ($CDCl_3$) δ 3.55 (s, 3 H, OCH_3), 6.8–7.6 (m, 11 H, aromatics), 8.36–8.56 (m, 2 H, aromatics). Anal. Calcd for $C_{21}H_{16}N_2O$: C 80.74; H, 5.16; N, 8.97. Found: C, 80.85; H, 5.05; N, 9.01.

Synthesis of 7a and 7c. LiMe (Fluka, 2 mmol) was added to imino derivative **10** (1 mmol in 20 mL of tetrahydrofuran) at room temperature and with stirring. After 2 h the reaction mixture was poured into 10% aqueous NH_4Cl (50 mL) and extracted with benzene. The separated benzene layer was evaporated to dryness, and the residue was taken up with ethanol (30 mL plus 1 mL of HCl) and refluxed for 4 h. The ethanol solution was evaporated to dryness and the residue taken up with 10% aqueous $NaHCO_3$ (50 mL) and benzene (50 mL). The benzene layer, dried on Na_2SO_4, was chromatographed on a silica gel column eluted with benzene. Amine **7a** was isolated in 65% yield: mp 128 °C (from ligroin, bp 100–135 °C); IR 1665 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ 1.75 (s, 3 H, CH_3), 3.79 (s, 3 H, OCH_3), 4.7 (br, 1 H, NH), 6.91 (d, 1 H, aromatics, J = 8.0 Hz), 7.09 (pseudo q, 1 H, aromatic, J = 8.0 Hz, J = 2.2 Hz), 7.34–7.6 (m, 6 H, aromatics). Anal. Calcd for $C_{16}H_{15}NO_2$: C, 75.86; H, 5.97; N, 5.53. Found: C, 75.76; H, 5.85; N, 5.45.

Amine **7c** was prepared in the same way by using LiPh (Fluka): yield 72%; mp 162 °C (from ligroin, bp 100–135 °C); IR 1670 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ 3.79 (s, 3 H, OCH_3), 4.9 (br, 1 H, NH), 6.91 (d, 1 H, aromatic, J = 8.0 Hz), 7.10 (pseudo q, 1 H, aromatic, J = 8.0, 2.2 Hz), 7.25–7.50 (m, 11 H, aromatics). Anal. Calcd for $C_{21}H_{17}NO_2$: C, 79.97; H, 5.43; N, 4.44. Found: C, 79.85; H, 5.45; N, 4.54.

Amines 7a and 7c from Nitroxides 5a and 5c. Nitroxide **5a** (1 mmol) and iron powder were refluxed for 5 min in 15 mL of acetic acid. After cooling, the reaction solution was filtered, and the filtrate was evaporated to dryness. The residue was taken up with benzene (50 mL) and 10% aqueous $NaHCO_3$ (50 mL). The benzene layer, chromatographed on a silica gel column eluted with benzene, gave **7a**: 85% yield; mp 128 °C. Starting from **5c** and working as described above, we isolated amine **7c**: 75% yield; mp 162 °C.

Nitroxides 5a and 5c from Amines 7a and 7c. Compound **7a** (100 mg) in $CHCl_3$ (20 mL) was treated with an equimolar quantity of *m*-chloroperbenzoic acid with stirring and at room temperature. After 30 min the reaction solution was chromatographed on preparative TLC of silica gel eluting with ethyl acetate–petroleum ether. The green fraction corresponded to nitroxide **5a**, which was extracted wiih chloroform and identified by its ESR signal.

Nitroxide **5c** was prepared from **7c** in the same way.

Registry No. 1a, 57309-27-0; **1b**, 57309-28-1; **1c**, 57309-29-2; **2a** (R^1 = Ph), 66312-78-5; **2a** (R^1 = Me), 72041-23-7; **2b** (R^1 = Ph), 66312-79-6; **2b** (R^1 = Me), 77494-93-0; **2c** (R^1 = Ph), 66312-80-9; **2c** (R^1 = Me), 77494-94-1; **3a** (R^1 = Ph), 66312-81-0; **3a** (R^1 = Me), 72041-22-6; **3b** (R^1 = Ph), 66312-82-1; **3b** (R^1 = Me), 77494-95-2; **3c** (R^1 = Ph), 66312-83-2; **3c** (R^1 = Me), 77494-96-3; **4a** (R^1 = Ph), 72041-28-2; **4a** (R^1 = Me), 72041-24-8; **4b** (R^1 = Ph), 77494-97-4; **4b** (R^1 = Me), 77494-98-5; **4c** (R^1 = Ph), 77494-99-6; **4c** (R^1 = Me), 77495-00-2; **5a**, 77495-01-3; **5b**, 77495-02-4; **5c**, 77495-03-5; **6a**, 77495-04-6; **6b**, 77495-05-7; **6c**, 77495-06-8; **7a**, 77495-07-9; **7c**, 77495-08-0; **9**, 5883-96-5; **10**, 77495-09-1.