

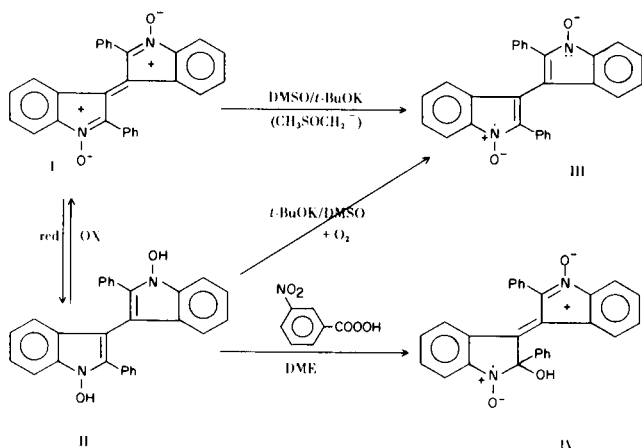
Anion and Neutral Nitroxides from 1-Hydroxy-2,2'-diphenyl-3,3'-biindole
and 1,1-Dihydroxy-2,2'-diphenyl-3,3'-biindole

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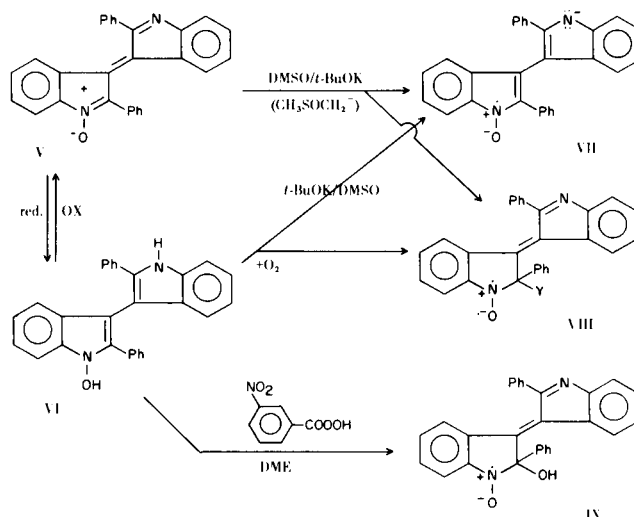
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In the course of our investigation into the chemistry of *N*-hydroxyindoles (1,2) we demonstrated that alkaline reduction of compound I or alkaline oxidation of compound II leads to the same anion nitroxide, III. Its structure follows the examination of the esr spectrum which shows hyperfine splitting constants due to the coupling of the unpaired electron with two equivalent nitrogen nuclei and with the eight benzo protons. Compounds V and VI were expected to show the same behaviour; but while reduction of V with the DMSO-potassium *t*-butoxide mixture [reducing agent being the anion $\text{CH}_3\text{SOCH}_2^-$ (3)] leads largely to anion nitroxide VII in a similar fashion (see Figure 1 and the explanation given therein), the same

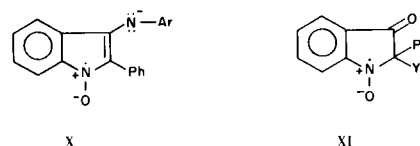


radical was not obtained during the alkaline oxidation of VI. Structure VII was attributed to the radical obtained during the reduction of V by comparison with analogous radicals in the series of aryliminoindoles, (e.g. X). In all these cases a simple spectrum which consisted essentially of three lines with further splittings not evaluated, was observed (2), corresponding to the spectrum appearing in the right part of Figure 1. The different spectrum obtained in the alkali oxidation of VI (Figure 2) can be attributed to radical VIII because of its higher nitrogen hyperfine splitting constant of 9.65 gauss, calling for a non-aromatic ring; we find a good analogy to radical VIII in the previously reported spectrum of radical XI (5). On the other hand, it has been shown (4,5) that in aromatic indole and pyrrole-type nitroxides the nitrogen hyperfine splitting



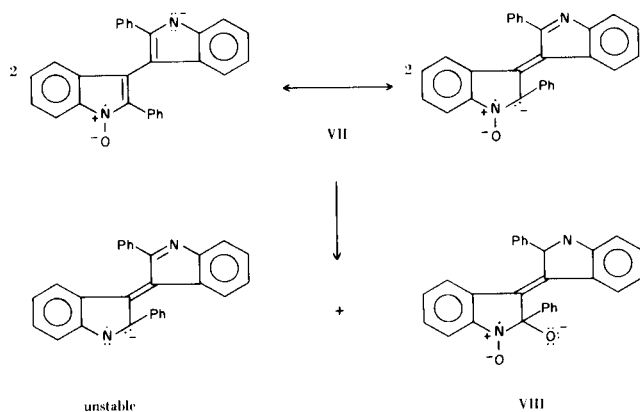
constant has values not exceeding *ca.* 6 gauss, while *ca.* 9-10 gauss are reported for indoline-type nitroxides.

As can be seen, reduction of V leads to two different radicals, as the spectrum in Figure 1 shows. While the stronger signals (right side of the spectrum) have already been discussed, the weaker set of signals (see left side of the spectrum) could be explained as arising from structure VIII, with an additional splitting of 1.00 gauss due to the two *m*-protons; The hyperfine splitting constants are identical to those shown by radical XI (5) where Y can stand for O^- or O^{0-} provided that base is present. The evidence therefore suggests that a disproportionation of radical VII can occur, following the path indicated. This sequence could also explain why the signal due to

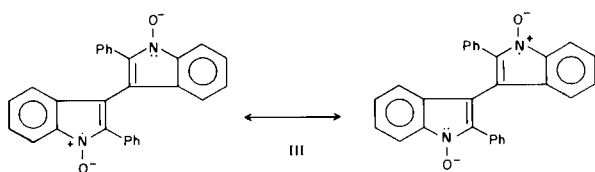


the radical VIII, that is the weaker in Figure 1, is much more intense after a few hours (see Figure 2), when radical III has completely disappeared.

The above results show that oxidation of II and VI does not follow the same course and that some differences are also found in the reduction of I and V. The reason for



this different behaviour can be found in the different symmetry of the molecules involved. In the case of radical III the equivalence of the two rings stabilizes the anion nitroxide radical through a mesomeric effect, while in the case of VII a further reaction can lead to the simultaneous presence of both VII and VIII, or of VIII alone.



Further support for the interpretation given above comes from the observation that the oxidation of II and VI with *m*-nitroperbenzoic acid in degassed dioxane leads to radicals IV and IX (see Figure 3), which show the same hyperfine splitting constants as the corresponding anion VIII.

All the spectroscopic parameters discussed in the work are reported in the Table.

TABLE

RADICALS	H F S C	REFERENCE
III		(2)
IV - IX	$a^N = 9.35$; $a^H = 3.00, 3.00$; $a^H = 1.00, 1.00$	oxidation of II and VI with <i>m</i> -NO ₂ -perbenzoic acid
VII	$a^N \sim 5$ gauss	alkaline reduction of V
VIII	$a^N = 9.65$; $a^H = 3.00, 3.00$; $a^H = 1.00, 1.00$	alkaline oxidation of VI or alkaline reduction of V

EXPERIMENTAL

Starting Compounds

Compounds I (6), II (6), V (1) and VI (1) were prepared by the previously published methods; *m*-nitroperbenzoic acid and potassium *t*-butoxide were commercial compounds and were used with-

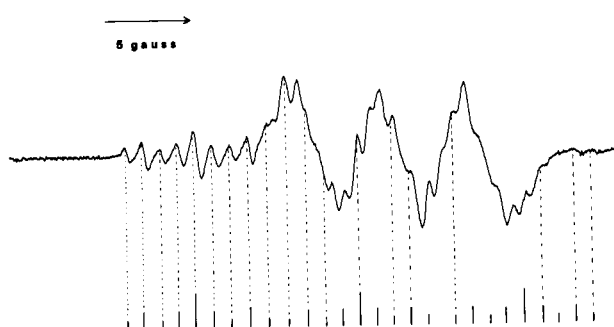


Fig. 1. Esr spectrum obtained during the reduction of 2,2'-diphenyl- $\Delta^{3,3'}$ -bi-3*H*-indole 1-oxide. In the bottom part of the figure the spectrum attributed to radical VIII has been emphasized.

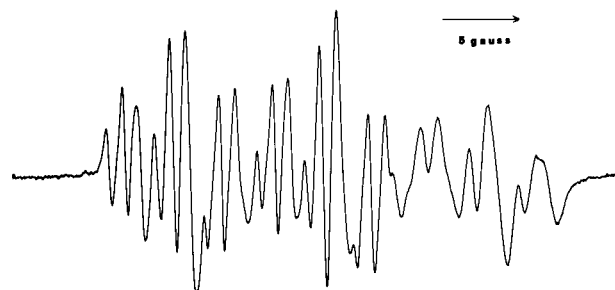


Fig. 2. Same sample as Figure 1, when observed after a few hours. The same spectrum has been observed during the oxidation of 1-hydroxy-2,2'-diphenyl-3,3'-biindole, and attributed to radical VIII.

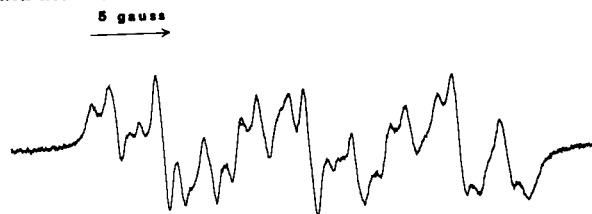


Fig. 3. Esr spectrum obtained during the oxidation of 1,1'-dihydroxy-2,2'-diphenyl-3,3'-biindole or 1-hydroxy-2,2'-diphenyl-3,3'-biindole with *m*-nitroperbenzoic acid in DME and attributed to radicals IV and IX.

out any further purification. DMSO, DME and dioxane were distilled and dehydrated by methods reported in the literature.

Preparation of the Radicals.

Radicals were generated directly in the cavity of the esr spectrometer using a Varian flat cell for aqueous samples and a V-type inverted cell previously described (3). For reduction reactions the cell was carefully deoxygenated with a 30 minute stream of prepurified nitrogen before the reactants were mixed. In oxidation reactions a small amount of air was allowed to enter the cell after the previous operation was performed.

Spectra

All esr spectra were recorded on a Varian E-4 Electron Spin Resonance spectrometer at room temperature.

REFERENCES

- (1) P. Bruni and M. Poloni, *Gazz. Chim. Ital.*, **100**, 1119 (1970).
- (2) P. Bruni and M. Colonna, *Tetrahedron*, **29**, 2425 (1973).
- (3) G. A. Russell, E. G. Janzen and E. T. Strom, *J. Am. Chem. Soc.*, **86**, 1807 (1964).
- (4) R. Ramasseul and A. Rassat, *Bull. Soc. Chim. France*, 4330 (1970).
- (5) G. A. Russell, C. Myers, P. Bruni, F. A. Neugebauer and R. Blankespoor, *J. Am. Chem. Soc.*, **92**, 2762 (1970).
- (6) M. Colonna and P. Bruni, *Gazz. Chim. Ital.*, **95**, 1172 (1965).