

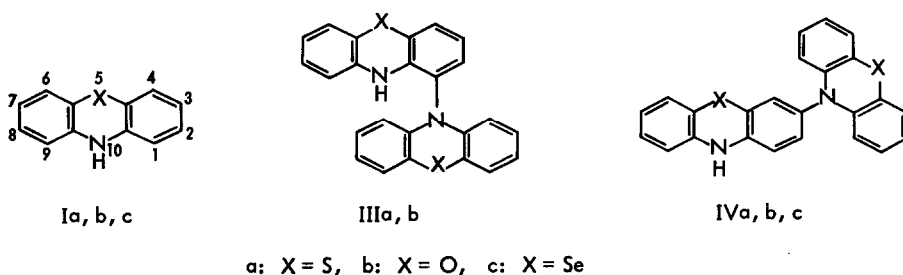
OXIDATION OF PHENOTHIAZINE, PHENOXAZINE, AND PHENOSELENAZINE
WITH DIMETHYLSULFOXIDE-ACETIC ANHYDRIDE (1)

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The oxidation of various alcohols to the corresponding carbonyl compounds by a mixture of dimethylsulfoxide and acetic anhydride has been suggested to proceed via an ionic intermediate (2, 3), but the formation of a free radical under this condition has never been reported. The present paper reports that phenothiazine (Ia) and phenoxazine (Ib) produce neutral radicals in DMSO-Ac₂O mixture and give 1,10'-dimer (IIIa, b) and 3,10'-dimer (IVa, b) as radical decay products.



Phenothiazine Ia was dissolved in DMSO-Ac₂O under deoxygenated state at room temperature. The e.s.r. spectrum of the solution was observed with time. The intensity of the signal increased gradually, and became maximum in several hours; the spectrum after 20 hr. was shown in FIG.-1. This signal was assigned to a neutral phenothiazinyl radical (IIa) (4). The hyperfine splitting constants were determined as follows: $a^N = 7.08$, $a_{3,7}^H = 3.68$, $a_{1,9}^H = 2.69$, $a_{2,8}^H = 1.00$, and $a_{4,6}^H = 0.76$.

After standing for one week at room temperature, the reaction mixture was poured into water and the resulting products were separated by preparative thin layer chromatography (silica gel, petroleum ether—

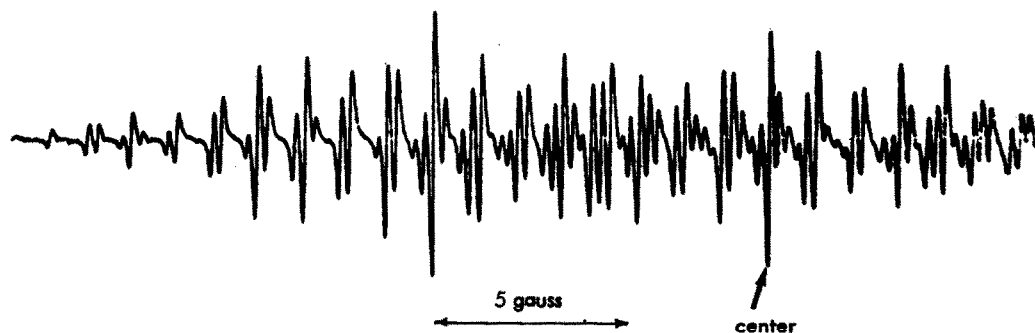
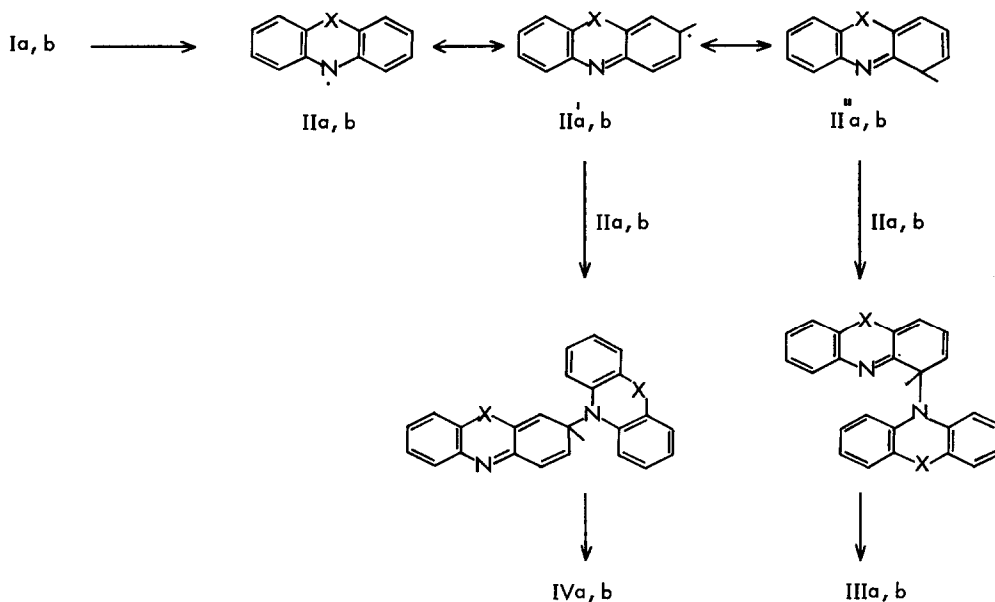


FIG.-1. The e.s.r. spectrum of the solution of Ia in DMSO-Ac₂O at room temperature after 20 hr.

ether = 2:1 v/v). There were obtained IIIa (3%), IVa (42%), V (14%) and VI (12%).

The structure of IIIa (mp 154-155°C) was confirmed on the basis of the following data: Anal. Calcd. for C₂₄H₁₆N₂S₂: C, 72.69; H, 3.97; N, 7.07; S, 16.17; mol wt, 396.54. Found: C, 72.49; H, 3.97; N, 7.19; S, 16.32; mol wt, 396 (from boiling point elevation). I.R. (nujol): 3365 cm⁻¹ (N-H), 762 cm⁻¹ (vicinally trisubstituted benzene ring) (5). The compound IVa (mp 198-199°C) was identified with 3,10'-biphenothiazine by mixed melting point (6). Compounds V (greenish powder, mol wt = 618) and VI (greenish powder, mol wt = 814), whose purifications were unsuccessful, may be a trimer and a tetramer of Ia, respectively.

The ratio of IIIa to IVa can be explained by the difference in free electron densities between 1- and 3-position of Ia which are clearly seen from hyperfine splitting constants, $a_{1,H}^H$ (2.69) and $a_{3,H}^H$ (3.68), and by the steric hindrance at 1-position of Ia. No formation of 10,10'-isomer may be due to the steric hindrance at 10-position of Ia. Accordingly, the reaction mechanism is proposed as follows:



Oxidation of phenoxazine (Ib) under the same condition gave similar results to that of Ia. The e.s.r. signal of the solution of Ib was more intensive than that of Ia as shown in FIG.-2. This signal was also assigned to a neutral phenoxazinyl radical (IIb), and hyperfine splitting constants were determined: $a^N = 7.73$, $a_{3,7}^H = 4.02$, $a_{1,9}^H = 3.01$, $a_{2,8}^H = 0.93$, and $a_{4,6}^H = 0.76$. The reaction mixture of Ib gave IIIb (15%), IVb (20%) and a complex mixture (VII) after standing for two days at room temperature. The compounds IIIb (mp 264-265°C) and IVb (mp 204-206°C) were identical with 1,10'- and 3,10'-biphenoxazine obtained by Musso's method (7), respectively. Thus, the oxidation of Ib can be concluded to proceed via a pathway similar to that of Ia, but higher ratio of IIIb to IVb than that of IIIa to IVa suggests that the steric hindrance at 1-position of IIb is smaller than that of IIa.

On the other hand, the e.s.r. signal of the solution of phenoselenazine (Ic) was too weak to be assigned. Similar treatment of the reaction mixture of Ic after one week gave a small amount of IVc (mp 216-217°C) and a major amount of polymer mixture (VIII). The structure of IVc (Anal. Calcd. for $C_{24}H_{16}N_2Se_2$: C, 58.79; H, 3.29; N, 5.71; mol wt, 490.30. Found: C, 58.58; H, 3.38; N, 5.40; mol wt, 455) was established by the fact that it gave N,N,N'-triphenyl-p-phenylenediamine on the reduction with Raney Nickel. Further purification of VIII (greenish powder, mol wt = 1098) was unsuccessful. These results suggest that phenoselenazinyl radical (IIc) is unstable compared with IIa and IIb.

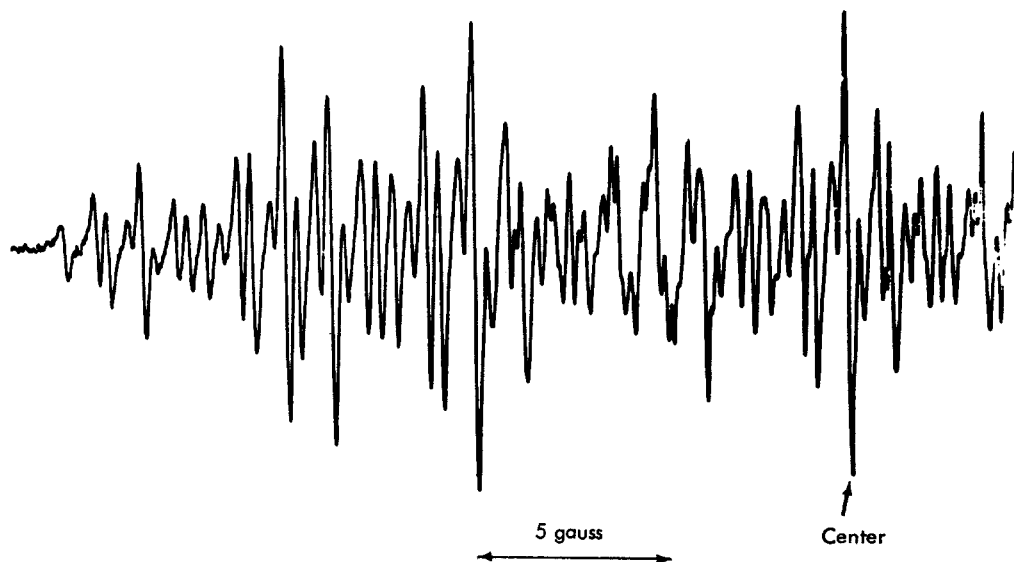


FIG.-2. The e.s.r. spectrum of the solution of Ib in DMSO-Ac₂O at room temperature after one hr.

Conclusively, it is proposed that oxidation of Ia, Ib and Ic with DMSO-Ac₂O proceeds via neutral radicals, whose stabilities are arranged in the following order: Ib > Ia > Ic, and the formation of products (III, IV) can be explained by free electron densities and steric effects at 1- and 3-positions of free radical intermediates (II).

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