FREE AZOXY RADICALS FROM BENZOQUINOLINES

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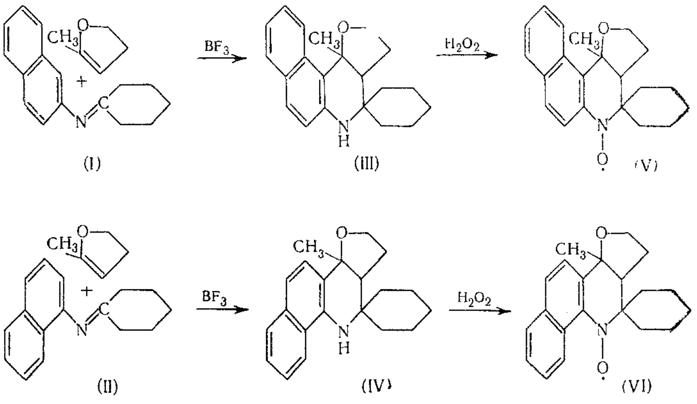
Previously, we had shown that the 2-spirocyclohexyl derivatives of tetrahydroquinolines when oxidized with hydrogen peroxide in the presence of sodium tungstate give stable azoxy radicals [1, 2]. In the present study, we synthesized the benzo derivatives of some 2-spirocyclohexyl-1,2,3,4-tetrahydroquinolines and from them the corresponding stable paramagnetic azoxy radicals. The condensation of cyclohexylidene-β-naphthylamine (I) and cyclohexylidene-α-naphthylamine (II) with 2-methyl-4,5-dihydrofuran in the presence of BF_3, proceeding in accordance with the diene synthesis scheme, respectively, gave as adducts the hydrogenated furoquinolines (III) and (IV), which then by the previously described method [2] were oxidized to azoxy radicals (V) and (VI).



2,2,4-Trimethyl-1,2-dihydro-5,6-benzoquinoline (VII) was oxidized under analogous conditions. Here the azoxy radical was obtained, which was recorded via the EPR spectrum, but proved to be unstable and was not isolated in the pure state.

The superfine structures of radicals (V) and (VI), and also of the radical obtained by the oxidation of (VII), in benzene solution are identical and represent a triplet (Fig 1), caused by the isotropic interaction of the unpaired electron with the nucleus of nitrogen N^{14}. The splitting between the components in the triplet is $a_N = 11.6 \pm 0.2$ ε, and is approximately equal to the constant of the superfine interaction a_N, found for the corresponding paramagnetic mononuclear derivatives [1, 2]. As a result, a change in the system of conjugation in the azoxy radicals of the hydrogenated quinoline series is practically without effect on the change in the electron density of the unpaired electron in the s-state attached to the nitrogen atom.

EXPERIMENTAL

Cyclohexylidene-α-naphthylamine (II). A solution of 71.7 g of α-naphthylamine and 58.8 g of cyclohexanone in 400 ml of benzene was heated under reflux in a flask equipped with a Dean-Stark trap until the liberation of water ceased. Fractional distillation gave 66 g (59%) of (II) with b.p. 140-141° 1.5 mm); m.p. 58-59°. Found %: C 85.31, 85.33; H 7.23, 7.25. $C_{16}H_{17}N$. Calculated %: C 86.05; H 7.67.

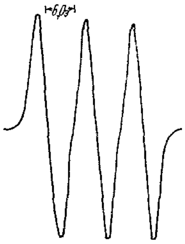


Fig. 1. EPR spectrum of radicals (V) and (VI) in benzene solution in the absence of oxygen.

Cyclohexylidene-β-naphthylamine (I). Operating in the same manner as before, we obtained (I) (65% yield) with b.p. 138-140° (1.5 mm); n_D^{20} 1.6320. Found %: C 85.37, 85.49; H 7.84, 7.90. Both (I) and (II) are easily hydrolyzed by atmospheric moisture.

4-Methyl-2-spirocyclohexyl-5,6-benzo-3,4:3',2'-tetrahydrofurano-1,2,3,4-tetrahydroquinoline (III). To a solution of 30.4 g of (I) in 50 ml of benzene was added 0.5 ml of BF_3 etherate, and then 15 g of 2-methyl-4,5-dihydrofuran. Here, the temperature of the reaction mixture rose from 22 to 85°. When the temperature had dropped to 23°, the mixture was washed with 10% NaOH solution and then dried over potassium carbonate. Fractional distillation gave 26 g (63.4% of theory) of (III) with b.p. 200-204° (0.1 mm); m.p. 121 to 122° (from alcohol). Found %: C 81.81, 81.90; H 8.20, 8.37. $C_{21}H_{15}NO$. Calculated %: C 82.04; H 8.20.

4-Methyl-2-spirocyclohexyl-7,8-benzo-3,4:3',2'-tetrahydrofurano-1,2,3,4-tetrahydroquinoline (IV). To a solution of 33.5 g of (II) in 50 ml of benzene was added 0.5 ml of BF_3 etherate, and then 12.6 g of 2-methyl-4,5-dihydrofuran was added dropwise in 10 min. The temperature of the reaction mixture rose from 18 to 48°. The mixture was stirred for 1 h at 50°, after which it was worked up as described in the preceding experiment. Fractional distillation gave 14 g (30% of theory) of (IV) with b.p. 213-220° (0.1 mm). Found %: C 81.54, 81.46; H 8.13, 8.34. $C_{21}H_{15}NO$. Calculated %: C 82.04; H 8.20.

4-Methyl-2-spirocyclohexyl-5,6-benzo-3,4:3',2'-tetrahydrofurano-1,2,3,4-tetrahydroquinolin-1-oxyl (V). To a solution of 2 g of (III) in 100 ml of methanol were added 0.1 g of sodium tungstate, 0.05 g of Trilon B,and 2 ml of 30% hydrogen peroxide solution. After a day the alcohol was vacuum-distilled, and the reaction mixture was extracted with benzene. The benzene extract, dried over Na_2SO_4, was passed through a chromatographic column (l = 400 mm, d = 20 mm), filled with Al_2O_3. The red-colored chromatographic zone was eluted. After evaporation of the benzene the solid product was recrystallized twice from methanol. We obtained 0.9 g (42.9% yield) of radical (V) as bright red needles with m.p. 147-148°. Found %: C 78.02; H 7.51; N 4.51; spins/M $5.1 \cdot 10^{23}$. $C_{21}H_{24}NO_2$. Calculated %: C 78.25; H 7.45; N 4.35; spins/M $6.02 \cdot 10^{23}$.

The reduction of radical (V) with phenylhydrazine under the previously described conditions [2] gave the corresponding hydroxylamine with m.p. 151-152° (from methanol). Found %: N 4.48. $C_{21}H_{25}NO_2$. Calculated %: N 4.32.

4-Methyl-2-spirocyclohexyl-7,8-benzo-3,4:3',2'-tetrahydrofurano-1,2,3,4-tetrahydroquinolin-1-oxyl (VI). Quinoline (IV) was oxidized under conditions analogous to those described above. The free radical (VI) was isolated by chromatographing on a column, filled with Al_2O_3, and was obtained as a bright red viscous oil. Found %: C 79.67; H 7.64; N 4.31; spins/M $5.0 \cdot 10^{23}$. $C_{21}H_{24}NO_2$. Calculated %: C 78.25; H 7.45; N 4.35; spins/M $6.02 \cdot 10^{23}$. Chromatographing on a plate (Al_2O_3, II activity, hexane + 20% acetone) revealed the presence of a small amount of the starting quinoline (IV), R_f 4.64; for radical (VI) R_f 2.64.

CONCLUSIONS

The 5,6- and 7,8-benzo derivatives of 4-methyl-2-spirocyclohexyl-3,4:3',2'-tetrahydrofurano-1,2,3,4-tetrahydroquinoline and their paramagnetic N-oxides were synthesized. A study was made of the paramagnetic absorption spectra of the free radicals, which are bezoquinoline derivatives.

LITERATURE CITED

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