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## Abstract

## Full Text

## CHEMISTRY

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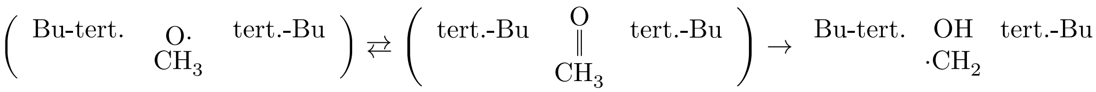
# THE E.P.R. SPECTRUM AND REARRANGEMENT OF THE RADICAL FORMED IN THE OXIDATION OF IONOL-$CD_3$

In a previous paper (1) it was shown, using deuterium labeling in the hydroxyl group, that the phenoxyl radical (I) formed upon oxidation of 2,6-di-*tert*-butyl-4-methylphenol (ionol) rearranges into the benzyl radical (II), with migration of hydrogen from the para-methyl group to oxygen:



$$\left(\text{Bu-tert.}\ \underset{\text{CH}_3}{\text{O}\cdot}\ \text{tert.-Bu}\right) \rightleftarrows \left(\text{tert.-Bu}\ \overset{\text{O}}{\underset{\text{CH}_3}{\|}}\ \text{tert.-Bu}\right) \rightarrow \text{Bu-tert.}\ \underset{\cdot\text{CH}_2}{\text{OH}}\ \text{tert.-Bu}$$

(I, II)

For further confirmation of this rearrangement, reverse labeling of the para-methyl group with deuterium was used. To obtain ionol containing deuterium in the methyl group, we used the method of isotopic hydrogen exchange with a solution of $KND_2$ in liquid $ND_3$ (2), taking into account that the mobility of hydrogen in the $CH_3$ group attached to the aromatic ring is considerably higher than in the *tert*-$C_4H_9$ group and in the ring (3). The reaction must be carried out under comparatively severe conditions, since in an ammoniacal solution of potassium amide ionol is converted into the corresponding phenolate, and the presence of a negative charge in the substance should hinder its hydrogen exchange with the base (4). For 1 g of ionol, 15 ml of a 0.5 $N$ solution of $KND_2$ in $ND_3$ was taken and heated for 24 hours at 100°. The preparation was distilled twice in vacuo. Isotopic analysis of the water from combustion of the ionol (5) showed that it contained 11.5 atom % D.

E.P.R. spectrum of the phenoxyl radical of ionol-CD3

**Fig. 1.** E.P.R. spectrum of the phenoxyl radical of ionol-$CD_3$

In the IR spectrum of a 0.1 $M$ solution of ionol-$CD_3$ in $CCl_4$, in addition to all the bands present in undeuterated ionol (3650, 2850–3000 $cm^{-1}$, etc.), bands at 2070 and 2110 $cm^{-1}$ were found, corresponding to the $CD_3$ group. These frequencies, in agreement with calculated values, are $\sqrt{2}$ times smaller than the corresponding frequencies 2870 and 2960 $\mathrm{cm}^{-1}$ of the $CH_3$ group. Frequencies of the aromatic CD bond were not detected. Consequently, the methyl group contains more than 90% D. Upon oxidation of ionol-$CD_3$ (0.1 $M$ solution in $C_6H_6$) by means of $PbO_2$ in an evacuated system, the solution became yellow. In the IR spectrum of the solution of oxidized ionol-$CD_3$ in $CCl_4$, in addition to all the above-listed frequencies of phenol and the newly appearing frequency 1610 $\mathrm{cm}^{-1}$ of the $C=O$ group, we found a band at 2692 $\mathrm{cm}^{-1}$, corresponding to the OD group. This confirms–

undergoes rearrangement (I) → (II) with transfer of a deuterium atom from the methyl group to oxygen.

The EPR spectrum consists of 9 lines with an intensity ratio of 1 : 4.4 : 13 : 23 : 26 : 23 : 13 : 4.5 : 1 and with identical splitting between components, $a_1 = 1.8$ oersted (Fig. 1). Such a spectrum corresponds exactly to that found earlier ($^{6,7}$) for the phenoxyl radical of ionol-$CH_3$, if one takes into account that, upon substitution of hydrogen by deuterium in the $CH_3$ group, the splitting constant $a$ must change in proportion to the gyromagnetic ratio, so that

$$a_{\mathrm{H}}/a_{\mathrm{D}} = \mu_{\mathrm{H}} I_{\mathrm{D}}/\mu_{\mathrm{D}} I_{\mathrm{H}} = 6.5,$$

where $I$ are the spins and $\mu$ the magnetic moments of the nuclei. Therefore the quadruplet with $a_{\mathrm{CH_3}} = 12$ oersted for splitting by three methyl hydrogens with $I_{\mathrm{H}} = \frac{1}{2}$, observed in the phenoxyl radical ionol-$CH_3$ ($^{6,7}$), is transformed into a septet with $a_{\mathrm{CD_3}} = 1.8$ for ionol-$CD_3$ ($I_{\mathrm{D}} = 1$). The splitting by both meta hydrogens remains the same. Previously a value $a_{\mathrm{H}} = 1.8$ oersted had been found for it ($^{6,7}$). Since it coincides with $a_{\mathrm{CD_3}}$, the lines of the triplet splitting are superimposed on the lines of the septet. Altogether, as is easy to calculate, 9 equally spaced lines should be observed in the EPR spectrum, with an intensity ratio of 1 : 5 : 13 : 22 : 26 : 22 : 13 : 5 : 1, which agrees with that observed (Fig. 1).

We did not observe changes in the EPR spectrum analogous to those detected in ($^{6}$) upon further oxidation of ionol. After 1.5 hours the spectrum changes into a singlet of width 2.4 oersted.

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*Note: Figure translations are in progress. See original paper for figures.*

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