STUDY OF THERMAL DECOMPOSITION OF BENZOPINACOL DIPHENYL ETHER BY THE ESR METHOD

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Received February 21st, 1972

The ESR spectrum is analyzed for the phenoxydiphenylmethyl radical, formed during the thermal decomposition of benzopinacoldiphenyl ether at 110°C. The hyperfine splitting constants were determined. The spin densities were calculated for various conformations resulting from the twist of the phenyl groups out of the plane of the radical; the best agreement with the experimental data was achieved for the angle of twist, 20°. The effect of the phenoxy group upon the shape of the ESR spectrum is discussed.

The ESR spectra of various diphenylmethyl[1,2], resp. diarylmethyl[3,4] radicals were studied and related to their conformation. The distribution of the unpaired electron in the radical is connected with the geometry of the latter, affecting thus also the hyperfine splitting constants. From that point of view, the phenoxydiphenylmethyl radical, formed on the thermal decomposition of benzopinacol diphenyl ether, was studied. The presence of the phenoxy group can affect interestingly the geometry of that radical.

EXPERIMENTAL

Triphenylmethyl can be easily obtained from triphenylmethyl chloride; the former is then oxidized to triphenylmethyl peroxide on air. This peroxide is rearranged to benzopinacol diphenyl ether in hot xylene[5,6]. A yellow solution is formed on dissolving that substance in hexachlorobutadiene at 110°C, yielding a well-resolved spectrum in an ESR spectrometer. In accordance with the mechanism of decomposition of aromatic pinacols[5] and with Hartzel's and Huyser's observations[7] during the thermal destruction of benzyl compounds containing methoxy groups, benzopinacol diphenyl ether is expected to decompose in the ethane C—C bond with the formation of phenoxydiphenylmethyl radicals. The measurements were carried out on an ESR spectrometer 12X, AEG, at 110°C.

RESULTS AND DISCUSSION

Half of the experimental ESR spectrum of the phenoxydiphenylmethyl radical *I* is presented in Fig. 1*a*. The number of splitting constants and their approximate values followed from a preliminary analysis of the spectrum, based on the ESR spectrum

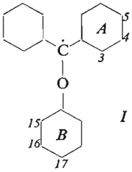
TABLE I

McLachlan's Spin Densities and Hyperfine Splitting Constants of Phenoxydiphenylmethyl Radical

Position	a_E^i, G		ϱ_i	a_T^i, G
	model M	model N		
3	-3.31	-3.31	0.119	-3.31
4	1.28	1.28	-0.042	1.17
5	-3.69	-3.51	0.127	-3.53
15	-0.18	-0.32	0.012	-0.33
16	0.18[a]	0.18	-0.006	0.17
17	—	-0.37	0.013	-0.36

[a] Sign indeterminate.

of the diphenylmethyl radical[8] and taking into account the value of the interaction parameter Q_{OH} for the hydroxyl proton. The values of the splitting constants were obtained by a detailed analysis based on the compilation of the theoretical model spectrum; they are given in Table I.



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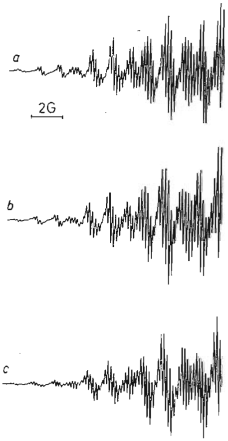

FIG. 1

ESR Spectrum of the Phenoxydiphenylmethyl Radical

The experimental spectrum exhibits a central line (Fig. 1*a*). This central line is preserved also on applying all the splitting constants of the two phenyl groups (A). The further structure of the spectrum is originated by the protons of the phenoxy group. The central line, apparent also from the beginning of the experimental spectrum, can be attained in the model spectrum under the assumptions as follows: *a*) one proton of the phenoxy group is replaced by some substituent, hence its interaction with the unpaired electron does not appear in the spectrum (model *M*); *b*) the splitting constants of the phenoxy group protons are such that a central line is formed by the superposition of the lines (model *N*). The splitting constants for the two models are given in Table I and the corresponding theoretical spectra in Fig. 1*b*,*c*. The hyperfine structure of the first three line groups at the start of the spectrum corresponds to the protons of the phenoxy group only.

It follows from the comparison of the spectra, Fig. 1, that model *M* is in a better conformity with the experimental spectrum. Model *N*, where the interaction of the *p*-proton with the unpaired electron is considered, disagrees with the experimental spectrum. This disagreement is apparent particularly from the side lines of the spectrum, determined by the protons of the phenoxy group. This shows that the unpaired electron interacts only with four protons of the phenoxy group. A possible theoretical model, leading to correct values of experimental splitting constants, is represented by a biradical[9], resulting from the reaction leading to the linking of radicals *I* in the *para* position of the phenoxy group, or by a radical with a substituent, not affecting the hyperfine structure of the spectrum, in the *para* position.

Table I lists the spin densities and hyperfine splitting constants, calculated by the McLachlan method[10] with the following parameters: $h_0 = 2{\cdot}4$, $k_{c-0} = 1$, $h_{c_1} = -0{\cdot}3$; the phenyl rings *A* are 20° twisted out of the plane of the radical. The hyperfine splitting constants were calculated from the McConnell relation[11] $a = Q\varrho$ with $Q = -27{\cdot}8$ G. The destruction of the ethane C—C bond proves to occur during the heating of benzopinacol diphenyl ether. Further reactions, however, proceed simultaneously, which leads to a changed interaction of the phenoxy group protons with the unpaired electron, as follows from model *M*.

Thanks are due to Professor D. Braun and Dr K. H. Becker for the supply of samples and for a valuable discussion.

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Translated by P. Adámek.