ESR STUDIES OF ALKYL ARYL KETYL RADICALS

Eva KUTEJOVÁ-MAŤAŠOVÁ, Andrej STAŠKO and Ľubomír MALÍK
Institute of Chemical Physics, Department of Physical Chemistry,
Slovak Institute of Technology, 880 37 Bratislava

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Reactions of R^1-substituted benzenecarboxylic acids (R^1 = H, Me, Et, and t-Bu) with R^2MgX (R^2 = Et and n-Pr) in the presence of nickel produce ketyl radicals R^1—Ar—$\overline{CO}^{\dot{-}}$—R^2. Average values of splitting constants of the protons in the aromatic nucleus are $\bar{a}_2 = \bar{a}_6 = 0{\cdot}48$ mT, $\bar{a}_4 = 0{\cdot}53$ mT, and $\bar{a}_3$, $\bar{a}_5 < 0{\cdot}12$ mT. In some cases for R^2 = n-Pr interaction of gamma protons is also observed with $\bar{a}_2 = 0{\cdot}04$ mT. The investigated substituents R^1, R^2 have no marked influence on distribution of spin density of the unpaired electron.

Recently considerable attention has been paid to study of the ketyl radicals formed by electron transfer from Grignard reagent to ketone[1-11]. Formation and stability of the radicals are affected by the Grignard reagent used, the respective ketone, solvent[4,5], and the presence of transition metal[10]. In our previous works[12-14] ESR was used to follow formation of the ketyl radicals in reactions of alkyl-substituted 2-hydroxybenzenecarboxylic acids with alkyl- or aryl-Grignard reagents in diethyl ether in the presence of nickel. We reinvestigated the influence of substituents on distribution of spin density of the unpaired electron and the role played by nickel in the mentioned reaction. The present paper complements this series by study of alkyl aryl ketyl radicals formed in reactions of substituted benzenecarboxylic acids (4-H, 4-Me, 4-Et, 4-t-Bu, and 3,5-di-t-Bu) with ethyl- or n-propylmagnesium bromides.

EXPERIMENTAL

All the chemicals used were rid of air oxygen and traces of humidity. 4-Methyl-, 4-ethyl, and 4-tert-butylbenzenecarboxylic acids were prepared by reaction of the respective Grignard reagent with solid carbon dioxide[15,16]. 3,5-Ditert-butylbenzenecarboxylic acid was obtained by catalytic oxidation of 3,5-ditert-butyltoluene. Benzenecarboxylic acid was a commercial product (Lachema, Brno). The Grignard reagents were prepared by standard procedure in diethyl ether under argon.

We used the experimental technique described in the previous papers[12-14]. In case of 4-ethyl-, 4-tert-butyl-, and 3,5-ditert-butylbenzenecarboxylic acids the ketyl radicals were generated direct in the ESR cells at room temperature, whereas in case of benzenecarbocylic acid and its 4-methyl

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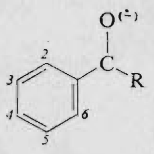
* Part XIV in the series Paramagnetic Products Formed in the Reactions of Organo-metallic Compounds; Part XIII: Organic Magn. Resonance *17*, 74 (1981).

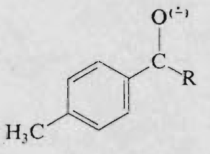
derivative the generation was carried out with cooling in a mixture of water and ice. Solution of the respective acid in diethyl ether (0·08 cm^3, 0·5 mol l^{-1}) under argon was treated subsequently with 0·24 cm^3 diethyl ether, 0·04 cm^3 0·1 mol l^{-1} nickel acetylacetonate in benzene solution and 0·08 cm^3 2 mol l^{-1} Grignard reagent. All the spectra were measured at room temperature with a Varian E-3 spectrometer and simulated with a computer Varian Spectra System 100.

RESULTS AND DISCUSSION

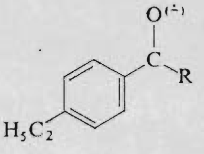
Reaction of R^1-substituted benzenecarboxylic acids with R^2MgBr in diethyl ether in the presence of nickel produces the below-mentioned relatively stable radicals *I – V* (*a, b, c*) which can be detected for a period of two to three days. The experimental and simulated spectra of the radicals are given in Fig. 1; Table I gives a list of the constants found by simulation and their assignment to the individual protons.



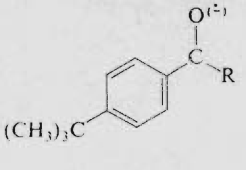
Ib



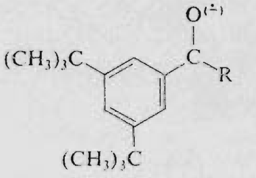
IIa,b



IIIa,b

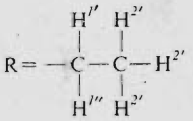


IVa,b



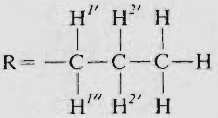
Va,b,c

a



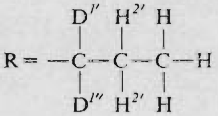
$\mathrm{R} = -\overset{\mathrm{H}^{1'}}{\underset{\mathrm{H}^{1'''}}{\mathrm{C}}}-\overset{\mathrm{H}^{2'}}{\underset{\mathrm{H}^{2'}}{\mathrm{C}}}-\mathrm{H}^{2'}$

b

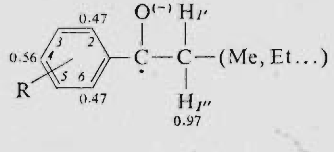


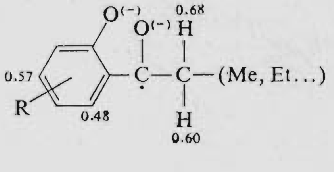
$\mathrm{R} = -\overset{\mathrm{H}^{1'}}{\underset{\mathrm{H}^{1'''}}{\mathrm{C}}}-\overset{\mathrm{H}^{2'}}{\underset{\mathrm{H}^{2'}}{\mathrm{C}}}-\overset{\mathrm{H}}{\underset{\mathrm{H}}{\mathrm{C}}}-\mathrm{H}$

c



$\mathrm{R} = -\overset{\mathrm{D}^{1'}}{\underset{\mathrm{D}^{1'''}}{\mathrm{C}}}-\overset{\mathrm{H}^{2'}}{\underset{\mathrm{H}^{2'}}{\mathrm{C}}}-\overset{\mathrm{H}}{\underset{\mathrm{H}}{\mathrm{C}}}-\mathrm{H}$



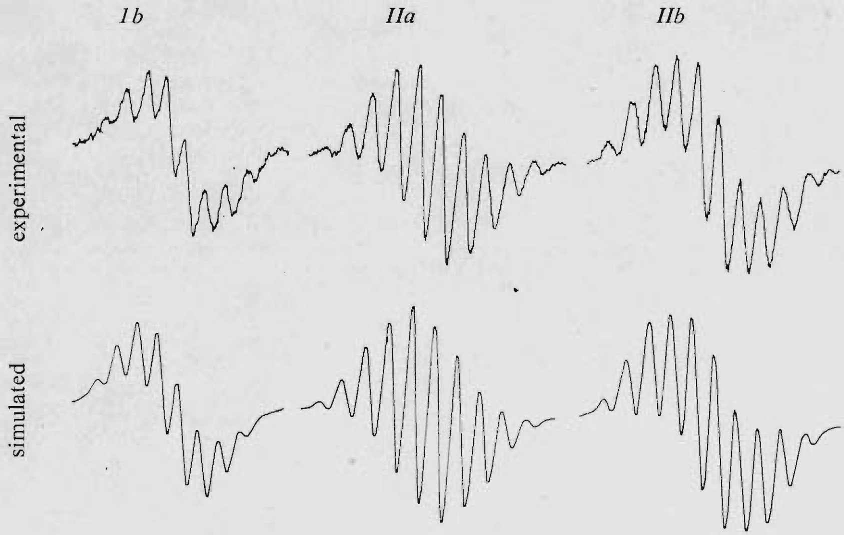


The splitting constants of structure *Ib* were assigned on the basis of known distribution of spin density of the unpaired electron in aryl-alkyl ketyl radicals and on the basis of deuteration. The two highest values were assigned to the protons of

TABLE I

Assignment of the splitting constants of the protons to the radical structures *I*—*V* (*a*,*b*,*c*)

Structure	Splitting constants, mT							
	a_2	a_3	a_4	a_5	a_6	$a_{1'}$	$a_{1''}$	$a_{2'}$
I *a*			little stable radical					
b	0·47	0·12	0·52	0·12	0·47	1·02	0·92	—
II *a*	0·47	0·12	0·60	0·12	0·47	1·05	1·05	—
b	0·49	0·12	0·61	0·12	0·49	1·00	0·90	0·04
III *a*	0·47	0·12	0·54	0·12	0·47	1·05	0·99	—
b	0·47	0·12	0·52	0·12	0·47	0·97	0·87	0·04
IV *a*	0·49	0·12	—	0·12	0·49	1·02	1·02	—
b	0·50	0·12	—	0·12	0·50	0·99	0·89	—
V *a*	0·47	—	0·56	—	0·47	1·07	1·07	—
b	0·47	—	0·52	—	0·47	0·98	0·98	—
c	0·47	—	0·52	—	0·47	0·20	0·20	—



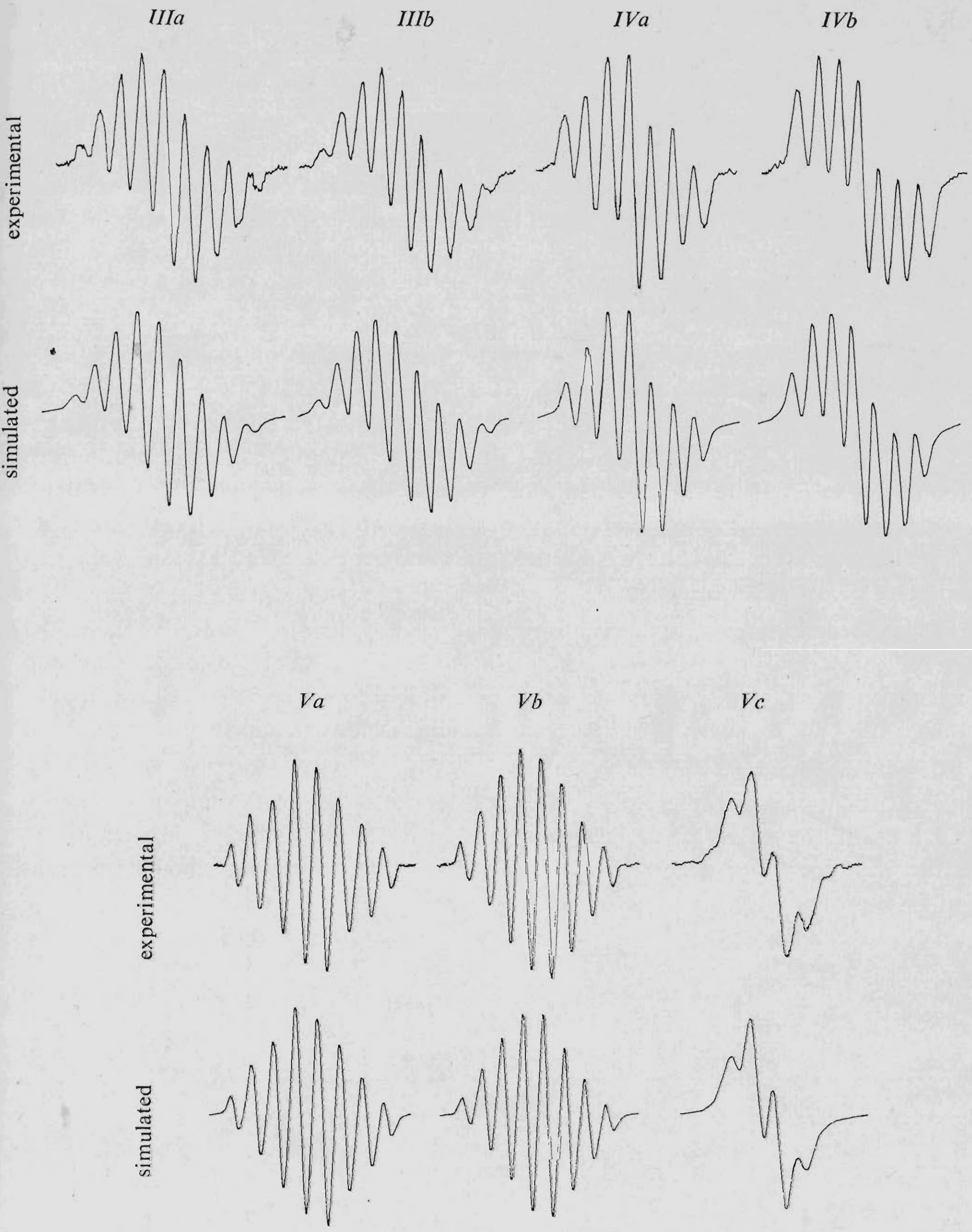


FIG. 1

Experimental and simulated ESR spectra of R^1—C_6H_4—$CO^{\dot{-}}$—R^2 radicals observed in reactions of R^1-substituted benzene carboxylic acids alkyl at beta position of ketyl group, the next highest value was assigned to *para* position, the next two ones to *ortho* position of benzene nucleus. This assignment was confirmed by the structures *II* to *V* showing the expected magnitude change of splitting constants and change of number of hyperfine splittings in the ESR spectra in accordance with change of substituent. In addition to it, in case of the well-resolved spectra of the structures *IIb* and *IIIb* we observed an indication of hyperfine splitting with the splitting constants $a \approx 0{\cdot}04$ mT (Fig. 2). On the basis of an analogous finding described in ref.[12] it is presumed that this hyperfine splitting is due to interaction of gamma protons of ketyl group with the unpaired electron. In analogy to aryl-alkyl radicals with oxyanion group[13], in this case we also found non-equivalency of β-hydrogen atoms, which is probably connected with hindered rotation of the alkyl groups bound to carbonyl group.

From Table I it follows that influence of the investigated alkyl groups on distribution of spin density of the unpaired electron is negligible. In this context it is interesting to compare the investigated alkyl-phenyl ketyl radicals without oxyanion group with the 2-oxyanion-phenyl ketyl radicals described in ref.[13]. These two types of radicals can be characterized by the following structures and average values of splitting constants of the protons.

The indexes given at individual positions of the structures *A*, *B* represent the values of splitting constants of the protons in mT. Striking is the effect of oxyanion group which, on going from structure *A* (without oxyanion) to structure *B* (with oxyanion), makes itself felt by lowering of values of the splitting constants of the beta protons of ketyl group ($a^{A}_{1'} = 1{\cdot}01$ mT → $a^{B}_{1'} = 0{\cdot}68$ mT, and $a^{A}_{1''} = 0{\cdot}97$ mT → $a^{B}_{1''} = 0{\cdot}60$ mT).

This effect can be explained by extended delocalization of the unpaired electron towards the oxyanion group, which results in decreased sigma-pi polarization in structures type *B* and decreased values of the splitting constants of the beta protons of ketyl group.

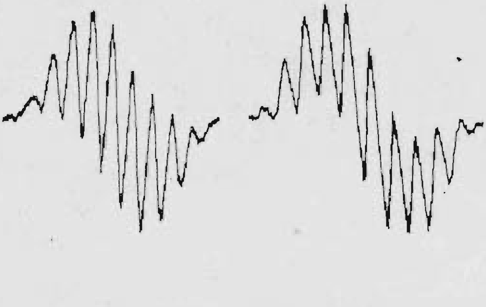


FIG. 2

Experimental spectra of the structures *IIb* and *IIIb* with an indication of hyperfine splitting of the gamma protons

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