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III. Hyperfine Splittings by Gamma Protons in ESR Spectra of Ketyl Radicals*

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The interaction of γ-protons with the unpaired electron in alkyl 1-[2-(oxide anion)-, 5-mono-*t*-butyl-, or 3,5-di-*i*-propyl-, or 3,5-di-*t*-butyl-substituted]-phenyl ketyl radicals was observed. The values of γ-coupling constants are 0.5–0.7 G if the alkyl is *n*-propyl or *n*-butyl and zero if the alkyl is ethyl. The values of the β- and γ-coupling constants depend on the type of solvent used.

INTRODUCTION

Previously (*1*, *2*) we reported on the formation of ketones via the reaction of 3,5-diisopropyl salicylic acid with Grignard reagents. In the presence of transition metals, the transfer of one electron from the Grignard reagent to the carbonyl group occurs to give ketyl radicals. The radicals obtained in this way we classified into several groups according to the character of ESR spectra and the type of Grignard reagents employed. For each group the radical structure was formulated and the coupling constants were assigned. The assignment was based on the systematic variation of Grignard reagents using their deuterated and nondeuterated analogs. The radicals formed by using ethyl, *n*-propyl, and *n*-butyl magnesium bromide were grouped together and described by one identical spectrum and by identical coupling constants. Investigating the spectra of radicals obtained when *n*-propyl and *n*-butyl Grignard reagents are used, we could now find new splittings which are not observed in the case of EtMgBr. These splittings are due to the interaction of the γ-protons of the alkyl with the unpaired electron.

EXPERIMENTAL

If not otherwise stated, all experiments were carried out at 20°C under a pure argon atmosphere. To the 0.5 *M* solution of the 3,5-alkyl-substituted salicylic acid in diethyl ether, nickel (II) chloride was added in such amounts that the final nickel concentration in the reaction mixture was about 10^{-4} *M*. The addition of 2.0 *M* solution of Grignard reagent in diethyl ether then followed so that the ratio RMgX:(acid) was 4. The 3,5-di-*i*-propyl salicylic acid (*3*), 5-mono-*t*-butyl salicylic acid (*4*), and 3,5-di-*t*-butyl salicylic acid (*5*) were prepared according to the procedure described in Ref. (*3*–*5*). The Grignard reagents were prepared by standard methods and C_2D_5MgBr was made as described in (*2*). The purified solvents were always dried with Grignard reagents

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* For Part II see Ref. (*1*).

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and redistilled prior to use. The spectra were recorded and simulated on a Varian E-3 Spectrometer equipped with a Varian Spectra System 100 Computer.

RESULTS AND DISCUSSION

Figure 1 shows both the experimental and simulated spectra obtained by measuring reaction mixtures of (a) 3,5-di-*i*-propyl salicylic acid [HDIPSA] with ethyl magnesium bromide [EtMgBr], (b) HDIPSA with deuterated EtMgBr, (c) HDIPSA with *n*-propyl magnesium bromide [*n*-PrMgBr], (d) HDIPSA with *i*-butyl magnesium bromide [*i*-BuMgBr], (e) 5-mono-*t*-butyl salicylic acid with *n*-PrMgBr and (f) 3,5-di-*t*-butyl salicylic acid with *n*-PrMgBr. The suggested structures of radicals involved in reactions

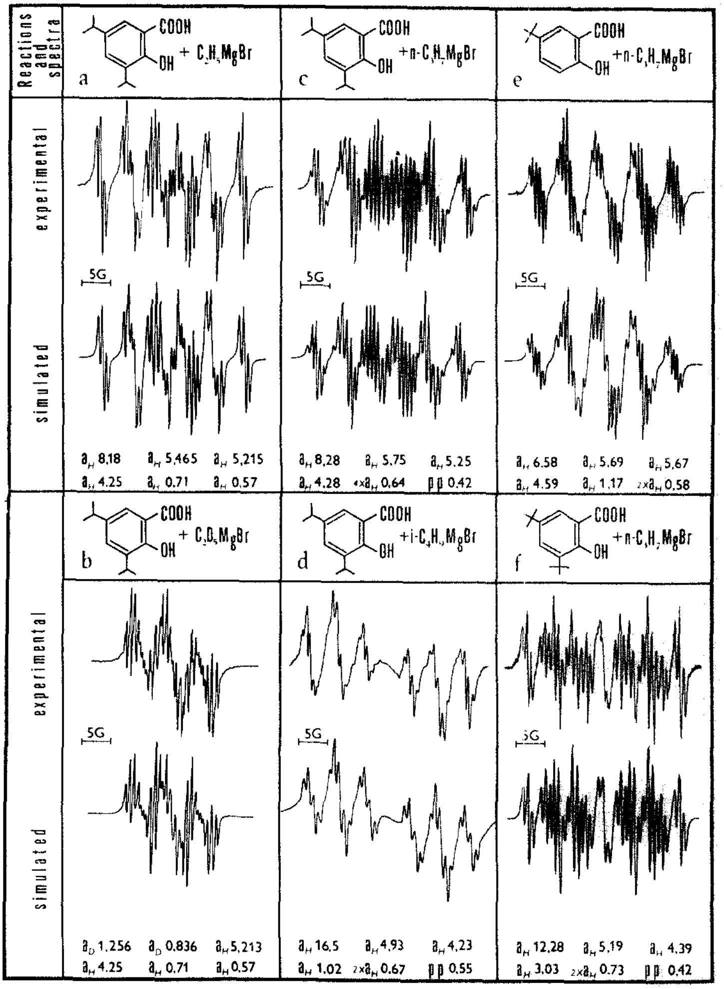
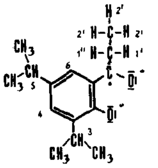
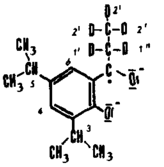
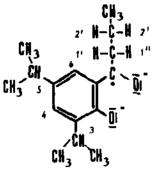
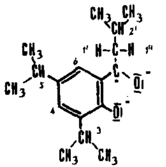
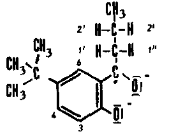
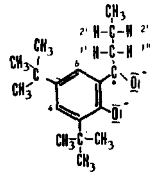


FIG. 1. Experimental and simulated ESR spectra of radicals formed by the reaction of differently substituted salicylic acids with Grignard reagents (a_H, a_D are the coupling constants, *pp*, the peak-to-peak widths of the simulated spectra expressed in gauss).

(a)–(f) and the assignments of the coupling constants are given in Table 1. The reasons for suggesting these radical structures have been discussed previously (*1*, *2*).

TABLE 1

STRUCTURES OF RADICALS AND THE ASSIGNMENT OF THE COUPLING CONSTANTS FOUND BY THE REACTION OF DIFFERENTLY SUBSTITUTED SALICYLIC ACIDS WITH GRIGNARD REAGENTS

Structure	coupling constants (Gauss)						
	a_3	a_4	a_5	a_6	$a_{1'}$	$a_{1''}$	$a_{2'}$
a 	0,71	5,215	0,57	4,25	8,18	5,465	-
b 	0,71	5,215	0,57	4,25	1,256	0,836	-
c 	0,64	5,25	0,64	4,28	8,28	5,75	0,64
d 	0,67	4,93	0,67	4,23	16,50	1,02	<0,55
e 	1,17	5,67	-	4,59	6,58	5,69	0,58
f 	-	5,19	-	4,39	12,28	3,03	0,73

The assignment of coupling constants a_3 and a_5 (0.5–0.7 G) to the protons of the isopropyl group (Table 1), a_4 and a_6 (4–6 G) to the ortho and meta protons respectively, as well as $a_{1'}$ and $a_{1''}$ (5–13 G) to the β-protons of the alkyl group becomes evident if spectra obtained using deuterated and nondeuterated EtMgBr (reactions a and b) are compared. More details justifying such an assignment were given in Ref. (*2*). If *n*-PrMgBr (reaction c) is applied instead of EtMgBr (reaction a), the spectrum c obtained can be described by coupling constants very similar to those in spectrum a, but spectrum c possesses two additional splittings of 0.64 G. These two splittings, characterized by $a_{2'}$ can be explained by the structure c only if interaction of the γ-protons with the unpaired electron is assumed. This interaction is obviously caused by the hindered rotation of methylene protons. The absence of the γ-interaction in the structure *a*, where the γ-protons are represented by the methyl group, is indicative of free rotation of the methyl protons. More evidence for the γ-interaction follows from spectra e and f. Spectrum e was simulated by one and spectrum f by two less splittings than spectrum a. This corresponds to the elimination of the interaction of either one or two protons belonging to the *i*-propyl group present in 3,5-position of the structure c, i.e. as if these positions were substituted by one *t*-butyl group, as in the case of structure e, or by two *t*-butyl groups, as in the case of structure f. Simplifying the spectra in this way, the coupling constant $a_{2'} = 0.73$ G corresponding to structure f can be unambiguously assigned to the interaction of γ-protons.

Upon substitution of the isopropyl group (structure c) for the *t*-butyl group (structure f), the coupling constants of aromatic protons do not change significantly while the difference between the two β-coupling constants of the alkyl group increases considerably. Remarkable changes of β-coupling constants were observed in the case of structure d, in which the alkyl group is the *i*-butyl group. The assignment of the coupling constants here is based on the following facts: Since the coupling constants of aromatic protons should have similar values for structures (a) to (d), we assigned the constants $a_3 = 0.67$ G, $a_4 = 4.93$ G, $a_5 = 0.67$ G and $a_6 = 4.23$ G in structure d to the aromatic protons (see Table 1). The remaining two coupling constants can only be assigned to the 1′ and 1″ protons of the *i*-butyl group. Such an assignment to the aromatic and to the alkyl protons was also confirmed by the radicals formed in the reaction of differently substituted salicylic acids with (CH_{3}–, C_2H_5–, C_2D_5–, and *n*-C_3H_7–) MgBr (*6*). The relatively high value of the coupling constant for the β-proton 1′ and the low value for the β-proton 1″ in structure d implies that the angle between the free π-electron and the σ-bond is nearly 0° for proton 1′ and nearly 90° for proton 1″. This suggests that the proton 1′ is localized almost perpendicularly and proton 1″ parallel to the plane of the aromatic ring. The coupling constant $a_{2'}$ of the γ-proton in the structure d is not evident from the spectrum and, therefore, should be smaller than 0.55 G as the peak-to-peak width of spectrum d is 0.55 G. The unequal resolution and intensity of the inside and outside lines, implying different relaxation times of the protons in such a system, deserve attention.

Values for the β- and γ-coupling constants similar to those observed for the branched *i*-butyl group (structure d) were also found in other structures if diethyl ether as solvent was replaced by di-*n*-butyl ether, benzene, or hexane. For example, the coupling constants $a_{1'} = 12.28$ G, $a_{1''} = 5.19$ G and $a_{2'} = 0.73$ G in structure f in diethyl ether change to $a_{1'} = 14.2$ G, $a_1'' = 1$ G and $a_{2'} < 0.4$ G if *n*-hexane is added to the reaction mixture. By variation of solvent and temperature, the spectra of radicals studied here often become asymmetrical, and contain more than the expected number of lines. Similar effects were also observed by other authors (*7*, *8*) and accounted for by the anisotropic molecular reorientation in solution.

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