Journal of Organometallic Chemistry, 92 (1975) 261–266

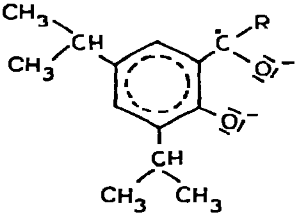
THE PARAMAGNETIC SPECIES PRODUCED IN THE REACTIONS OF TRANSITION METAL CHELATES WITH ORGANOMETALLIC REAGENTS

II*. THE STRUCTURE OF KETYL RADICALS FORMED BY THE REACTION OF THE DIISOPROPYLSALICYLATE LIGAND WITH GRIGNARD REAGENTS

A. STAŠKO, A. TKÁČ, L. MALÍK and V. ADAMČÍK
Institute of Chemical Physics, Slovak Technical University, 88037 Bratislava (Czechoslovakia)
(Received January 10th, 1975)

Summary

Grignard reagents form, by the reaction with nickel(II) diisopropylsalicylate, a ketyl radical, which is described by the following common structure:



(R = H, alkyl or Ph)

The reagents applied in these reactions were divided into the following six groups according to the type of spectra obtained: (1) hydrides, (2) CH_3MgI, (3) n-alkyl-MgBr, (4) s-alkyl-MgBr, (5) t-BuMgBr and (6) PhMgBr. The radical structure corresponding to each group was determined and the coupling constants found by means of simulation were assigned using non-deuterated and deuterated reagents.

Introduction

In our previous work [1] it was reported that the formation of stable radicals had been observed as a result of the reaction of nickel(II) diisopropylsalicylate $Ni(DIPS)_2$ with Grignard reagents RMgX in the molar ratio Mg/Ni > 6. We

---

* For Part I see ref. 1.

described the role of transition metal in these reactions, assumed the formation of a ketyl radical and suggested a reaction mechanism to explain the observed radical formation. In the work presented here we determined the structure of the assumed ketyl radicals. This was achieved by a systematic variation of the alkyl or aryl groups of the Grignard reagent and by the replacement of the non-deuterated groups by their deuterated counterparts.

In a similar reaction of Ni(DIPS)$_2$ with s-BuLi, the generation of radicals was explained by the oxidation of s-BuLi with transition metal ions with the formation of the butene cation radical [2]. On the other hand, in the reactions of Grignard reagents with a carbonyl group a transfer of one electron from the Grignard reagent to the carbonyl group [3-6] is very often proposed. The systematic investigations described here clarify the contribution of the alkyl or aryl group to the radical structure and enable us to formulate the structure of different radicals, which are formed by the reaction of Ni(DIPS)$_2$ with different RMgX. The results obtained here are in agreement with the reaction scheme given in our previous paper [1].

Experimental

The preparation of the reactants and the experimental techniques were described previously [1]. The deuterated Grignard reagents CD_3MgI, C_2D_5MgBr and C_6D_5MgBr were prepared from CD_3OH, C_2D_5OH and C_6D_6 (Isomerc, Berlin). $LiAlH_4$, $LiAlD_4$ and $NaAlH_2(OCH_2CH_2OCH_3)_2$ were obtained from Institute of Inorganic Synthesis ČSAV, Prague, and n-BuLi from A.G. Metallgesellschaft, Frankfurt a.M. The spectra were recorded and simulated on a Varian E-3 Spectrometer equipped with a Computer Varian Spectra System 100.

Results and discussion

The reaction of Ni(DIPS)$_2$ with different Grignard reagents, as well as with hydrides and n-BuLi, results in the formation of free radicals if the molar ratio Mg/(chelate ligand) > 3. According to the type of Grignard reagent used the radical spectra observed can be divided into 6 groups, each with a characteristic ESR spectrum as shown in Fig. 1.

It is obvious from Fig. 1 that the radical structure depends on the type of Grignard reagent employed. Similar spectra were obtained with similar reagents e.g. hydrides, n-alkyls and s-alkyls. On the other hand, with one type of Grignard reagent the spectral structure changes if diisopropylsalicylate is replaced by another chelate ligand such as acetylacetonate, as described before [1]. From these facts we concluded that the chelate ligand, as well as the hydride or the Grignard reagent, participates in the formation of the radical. To assign the interactions of the unpaired electron with the protons of the chelate ligand and the protons the reagents, we compared the spectra obtained if the non-deuterated reagents were replaced by their deuterated compounds. The measured spectra and their simulations for the case of the non-deuterated compounds are given in the upper part, and for the deuterated compounds in the lower part, of Fig. 1, respectively.

The simplest situation would be expected with hydrides, i.e. in group 1, where only a simple atom such as hydrogen or deuterium can be transferred from

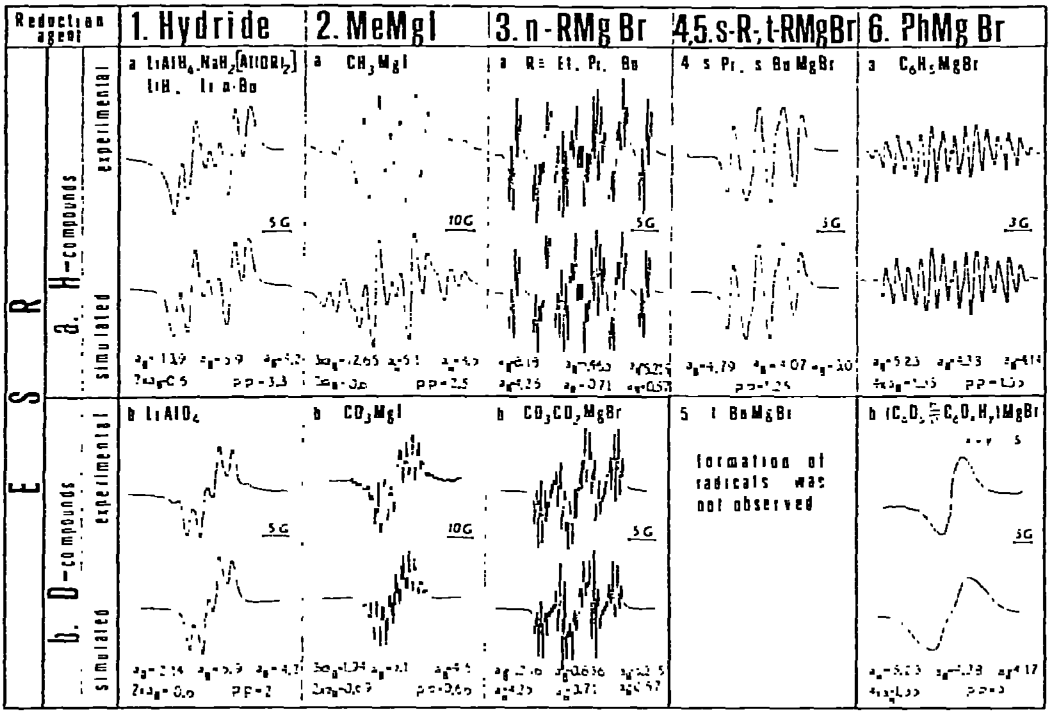


Fig. 1. Experimental and simulated ESR spectra of radicals formed by the reaction of nickel(II) diisopropylsalicylate with different deuterated and non-deuterated reagents (a_H, a_D are the coupling constants, pp the peak-to-peak widths of the simulated spectra, expressed in Gauss).

the reduction reagent to the chelate ligand. Spectrum 1a, corresponding to the application of $LiAlH_4$, was simulated by means of the following coupling constants of protons: $a_H = 13.9$, $a_H = 5.9$, $a_H = 4.2$ and $2 \times a_H = 0.6$ (all coupling constants given in this text are expressed in Gauss). The two constants having $a_H = 0.6$ are not evident from the spectrum measured at the given resolution, but we specify them here, as coupling constants of this order were found with reagents of groups 2 and 3. Using $LiAlD_4$ instead of $LiAlH_4$ spectrum 1b was obtained; this was simulated using the parameters of the non-deuterated compound 1a but exchanging one coupling constant for a proton having $a_H = 13.9$ with the corresponding parameter for deuteron, $a_D = 2.14$. From these experiments it was concluded that the hydrides contribute to the measured spectral structure with one hydrogen and that the remaining four protons come from the chelate ligand. The relatively high value of the coupling constant for the proton originating from hydride deserves attention.

The spectrum for group 2a, obtained using CH_3MgI, was simulated using coupling constants of four protons having similar values, as found for the chelate ligand in group 1 ($a_H = 5.1$, $a_H = 4.5$, and $2 \times a_H = 0.69$), and furthermore with coupling constants of three equivalent protons having $a_H = 12.65$, believed to originate from the methyl group. This is confirmed by spectrum 2b, which was measured replacing CH_3MgI by CD_3MgI. This spectrum of the deuterated radical

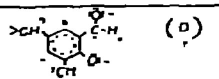
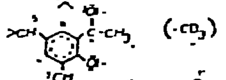
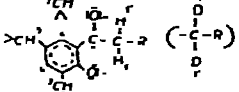
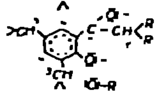
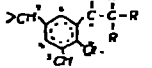
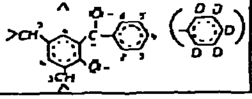
2b was simulated using parameters of the non-deuterated compound 2a, exchanging the coupling constants of three a_H = 12.65 protons with the corresponding constants of deuterons having a_D = 1.94. Again, the relatively high value for the coupling constant of the methyl protons is remarkable.

In group 3a identical spectra were obtained if Et-, n-Pr- or n-Bu-MgBr was applied. Spectrum 3a of the non-deuterated radical was simulated again using coupling constants of four protons (a_H = 5.215, a_H = 4.25, a_H = 0.71 and a_H = 0.57) having similar values to those assigned to the chelate protons in groups 1 and 2 and, furthermore, with coupling constants of two protons having a_H = 8.18 and a_H = 5.465. Analogously to groups 1 and 2, we assigned these two constants to the protons originating from the n-alkyl group. This assignment is confirmed by spectrum 3b, which we measured using C_2D_5MgBr instead of C_2H_5-MgBr. Spectrum 3b was simulated using the parameters for 3a replacing the coupling constants of two protons (a_H = 8.18 and a_H = 5.565) by the corresponding coupling constants of deuterons (a_D = 1.256 and a_D = 0.836). From these results it is obvious, that these two protons are those in the n-alkyl group. A remarkable feature is their lack of equivalence which is probably caused by the hindered rotation of the n-alkyl moiety.

The spectra measured by application of s-alkyl-MgBr reagents were simulated employing three coupling constants (a_H = 4.79, a_H = 4.07 and a_H = 3.0). Analogously to the results in the groups 1, 2 and 3 we assigned one coupling constant (a_H = 3.0) to the proton of the s-alkyl group ($\geq$C—H) and the remaining two coupling constants (a_H = 4.79 and a_H = 4.07) to the protons of the salicylate ligand (an alternative assignment is possible). In group 5, using t-BuMgBr, no formation of radicals was observed.

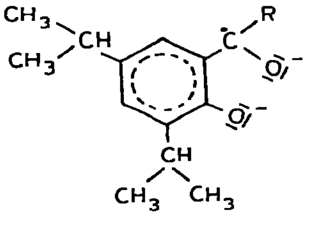
TABLE I

STRUCTURES OF RADICALS AND THE ASSIGNMENT OF THE COUPLING CONSTANTS FOUND BY REACTION OF NICKEL(II) DIISOPROPYLSALICYLATE WITH DIFFERENT GRIGNARD REAGENTS

group	Radical	a_3	a_4	a_5	a_6	a_{1H}	a_{1D}
1		0.6	5.9	0.6	4.2	13.9	2.14
2		0.69	5.1	0.69	4.5	12.65	1.94
3		0.71	5.215	0.57	4.25	8.18 5.465	1.256 0.836
4		<0.5	4.79	<0.5	4.07	3.0	
5		formation of radical was not observed					
6		<0.5	1.35	<0.5	1.35	a_2= 4.14 a_3= 4.38 a_4= 5.23 a_5=a_6= 1.35	exchange H⇌D

In group 6, using non-deuterated PhMgBr, we obtained spectrum 6a which was simulated by the following proton coupling constants: a_H = 5.23, a_H = 4.38, a_H = 4.14 and 4 × a_H = 1.35. With experiment 6b, using the deuterated phenyl compound, we could not obtain the expected information as exchange between the deuterons and the protons of the phenyl group took place; we therefore assume the resulting non-resolved spectrum 6b to be the sum of the differently-deuterated radical spectra. Spectrum 6b, obtained using the deuterated PhMgBr, is narrower than that obtained with the non-deuterated compound 6a. This indicates that the protons of the phenyl group participate in the formation of the radical structure. Our assignment of the coupling constants to the protons in the phenyl group and to the protons in the salicylate group, as given in the Table 1, is based on a common structure of the radicals, which is discussed below.

In our previous work [1] it was found that, by reaction of $Ni(DIPS)_2$ with RMgX or hydrides, the carboxyl group of salicylate is reduced to the carbonyl group with formation of the corresponding ketone or aldehyde. In these reactions we observed a radical whose generation was mediated by the transition metal. On the basis of the nature of the products formed during the reaction we suggested the generation of a ketyl radical and described it by the following common structure:



(R = H, alkyl, Ph)

This is in very good agreement with all the spectral data presented in Fig. 1. Structures corresponding to the different types of radicals and the assignments of their coupling constants are given in Table 1.

The comparison of the experimental and simulated spectra obtained using non-deuterated and deuterated reagents presented for groups 1, 2 and 3 in Fig. 1 shows that the assignment of the coupling constants to the protons in the salicylate ligand and to the protons in the applied reagents, as described in Table 1, is correct. The remarkably high values for the coupling constants of the protons from the methyl and n-alkyl group of the Grignard reagents implies the localization of these H's close to the ketyl group which agrees with the formulated structure of the ketyl radical. Also, the coupling constants (average 5 G for the *para* protons, 4 G for the *ortho* proton and about 0.6 G for the *meta* protons) of diisopropylsalicylate are in good agreement with the coupling constants which are known for similar structures. The decrease of the coupling constants (in Gauss) from the value for the aldehydic proton (a_H = 13.9) to the methyl (a_H = 12.65) n-alkyl (a_H = 8.18 and a_H = 5.465) and s-alkyl (a_H = 3.0) protons is also confirmed by common experience. Therefore we assigned the smallest coupling constant (a_H = 3.0) to the proton of s-alkyl and the remaining two coupling constants to the protons of the salicylate. This assignment cannot be proved at present as the corresponding deuterated compound is not available. Using t-BuMgBr in group 5 no formation of radical was observed, possibly due to steric hinderance of the bulky t-butyl group. In group 6, using PhMgBr, we obtained a spectrum which was simulated by means of the following coupling constants: $a_{\mathrm{H}} = 5.23$, $a_{\mathrm{H}} = 4.38$, $a_{\mathrm{H}} = 4.14$ and $4 \times a_{\mathrm{H}} = 1.35$. As the experiment with the deuterated phenyl group did not afford the necessary information, we based our assignment of the coupling constants on comparison of the different electronic densities caused by the electronegative substituents on the aromatic rings placed on both sides of the ketyl group. The delocalization of the unpaired electron on the substituted phenyl originating from the salicylate is less probable than that of the unsubstituted phenyl group originating from the Grignard reagent; we therefore suppose the highest spin population to be in the *para* position of the unsubstituted phenyl group and assign to this position the highest coupling constant ($a_{\mathrm{H}4'} = 5.23$). The two next highest coupling constants ($a_{\mathrm{H}6'} = 4.38$ and $a_{\mathrm{H}2'} = 4.14$) are assigned to the *ortho* protons of the phenyl group and, of the remaining four coupling constants ($4 \times a_{\mathrm{H}} = 1.35$), two are assigned to the *meta* protons of the phenyl group and two to the *ortho* and *para* protons of the salicylate residue. This assignment is confirmed by the experiments with the differently substituted phenyl Grignard reagents which we are now studying.

References

1 A. Staško, A. Tkáč, R. Přikryl and L. Malík, J. Organometal. Chem., 92 (1975) 253.
2 H.J.M. Bartelink, H.K. Ostendorf, B.C. Roest and H.A.J. Schepers, Chem. Commun., (1971) 878.
3 K. Maruyama, Bull. Chem. Soc. Jap., 37 (1964) 897.
4 G. Blomberg, H.H. Grootveld, T.H. Gerner and F. Bickelhaupt, J. Organometal. Chem., 24 (1970) 549.
5 R. Gelin, S. Gelin and A. De Hondt, Tetrahedron Lett., (1971) 4669.
6 T. Holm and I. Grossland, Acta Chem. Scand., 25 (1971) 59.