Intermediate radical products formed in the catalytic systems of nickel with organometallic compounds

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Contents

The investigations of paramagnetic products formed in the catalytic systems of nickel with organometallic compounds performed by e.s.r. and other methods in author's laboratory are summarized. This involves Ni(II), Ni(I), and Ni(0) species, new series of anion radicals of various chelate ligands and their products (β diketonates, carboxylates, sulfones, ketyl radicals, *etc.*). The influence of solvents, organometallic compounds, transition metals, and the counter ions of anion radicals on their stability and distribution of unpaired spin density is described. Oxido anion group in position 2 on benzene ring of aryl (Ar) and alkyl (R) ketyl radicals (Ar—, $^{-}$O—Ar—)CO$^{\dot{-}}$(Ar, R) shows an expressive push as well as pull effect. Nickel mediates the transfer of electron and stabilizes the intermediate products in form of their anion radicals. New method in the generation of anion radicals of various substrates by means of organometallic compounds was developed.

Приведен обзор результатов исследований парамагнитных продуктов, образующихся в каталитических системах никеля с металлоорганическими соединениями, проведенных методом ЭСР и другими методами в лаборатории автора. Эти системы включают соединения Ni(II), Ni(I) и Ni(0), новые виды анион-радикалов различных хелатных лигандов (таких как β-дикетонатов, карбоксилатов, сульфонов, кетил-радикалов и др.). Описано влияние растворителя, металлоорганического соединения, природы переходного металла и противоионов к анион-радикалам на их стабильность и распределение спиновой плотности непарного электрона. Оксильная группа в положении 2 бензольного кольца арил (Ar) или алкил (R) кетил-радикалов (Ar—, $^{-}$O—Ar—)CO$^{\dot{-}}$(Ar, R) вызывает значительный пуш-пул эффект. Никель способствует переносу электрона и стабилизирует промежуточные продукты в форме анион-радикалов. Разработан новый метод генерирования анион-радикалов различных субстратов посредством металлоорганических соединений.

1. Introduction

The increasing interest in the preparation of new, effective catalysts requires a detailed knowledge of the structure of their active centra, their function, and the pathways of their formation. Taking into account their low concentrations in the catalytic systems, the means to their direct observation are limited. Therefore our attention was focused on the e.s.r. and other spectroscopic investigations of the catalytic systems consisting of nickel(II) chelates and organometallic compounds, as these systems are widely employed in various reactions [1—4] and e.s.r. is a relatively sensitive method providing detailed information on various paramagnetic intermediates. The presented paper summarizes our work in this field for last few years.

2. Paramagnetic products in the reactions of nickel(II) chelates with organometallic compounds

2.1. Reduction of nickel(II) diisopropylsalicylate with Grignard reagents

The paramagnetic products formed in the reaction mixture of nickel(II) diisopropylsalicylate (NiDIPS$_2$) with Grignard reagents (RMgX) under the conditions as described in [5] depend on the mole ratio Mg:Ni as shown in Fig. 1. There are three regions of mole ratios, each with a characteristic e.s.r. signal.

The first region at the ratios Mg:Ni up to 4:1 is characterized by a singlet having $g_1 = 2.17$. The maximum observed concentration of paramagnetic species corresponds to 5 % nickel atoms present in the system. The appearance of singlet with g_1 is accompanied by the formation of a black precipitate, soluble in alcohol, giving Ni(II) solution. During the reaction with RMgX hydrocarbon RH is formed and simultaneously an absorption band at 1390 cm^{-1} characteristic in i.r. spectrum of the phenoxy group of salicylate ligand disappears.

At the mole ratios Mg:Ni = 4—7 the singlet having $g_1 = 2.17$ is replaced by a new singlet with $g_2 = 2.10$. It disappears when oxygen is brought into the reaction mixture, in contrast to signal with g_1. The maximum measured concentration of paramagnetic species with g_2 corresponds to 0.05 % nickel atoms added to the system.

When the mole ratio Mg:Ni>6 the signal having g_2 characteristic of the transition metal disappears and spectrum typical of free radicals with $g_3 = 2.004_2$ is observed. The maximum concentration of these radicals was 10^{-4} mol dm^{-3} and it corresponds to 0.3 % nickel atoms in the system. The hyperfine structure of this

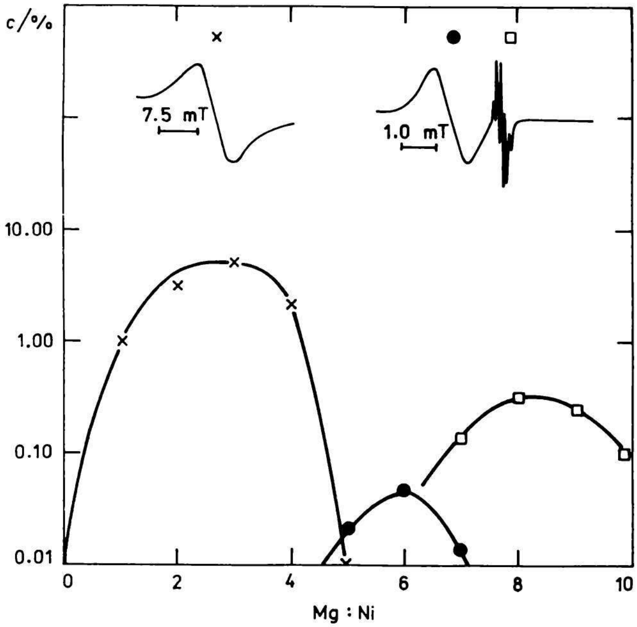


Fig. 1. Concentration of paramagnetic products at different mole ratios Mg:Ni.
× $g = 2.17$; ● $g = 2.1$; □ $g = 2.0042$.

radical product depends on the type of Grignard reagents as well as on the type of chelate ligand and will be discussed below.

Based on the separation and analysis of the reaction products [5] in the catalytic system the formation of the paramagnetic products was explained by means of Scheme 1.

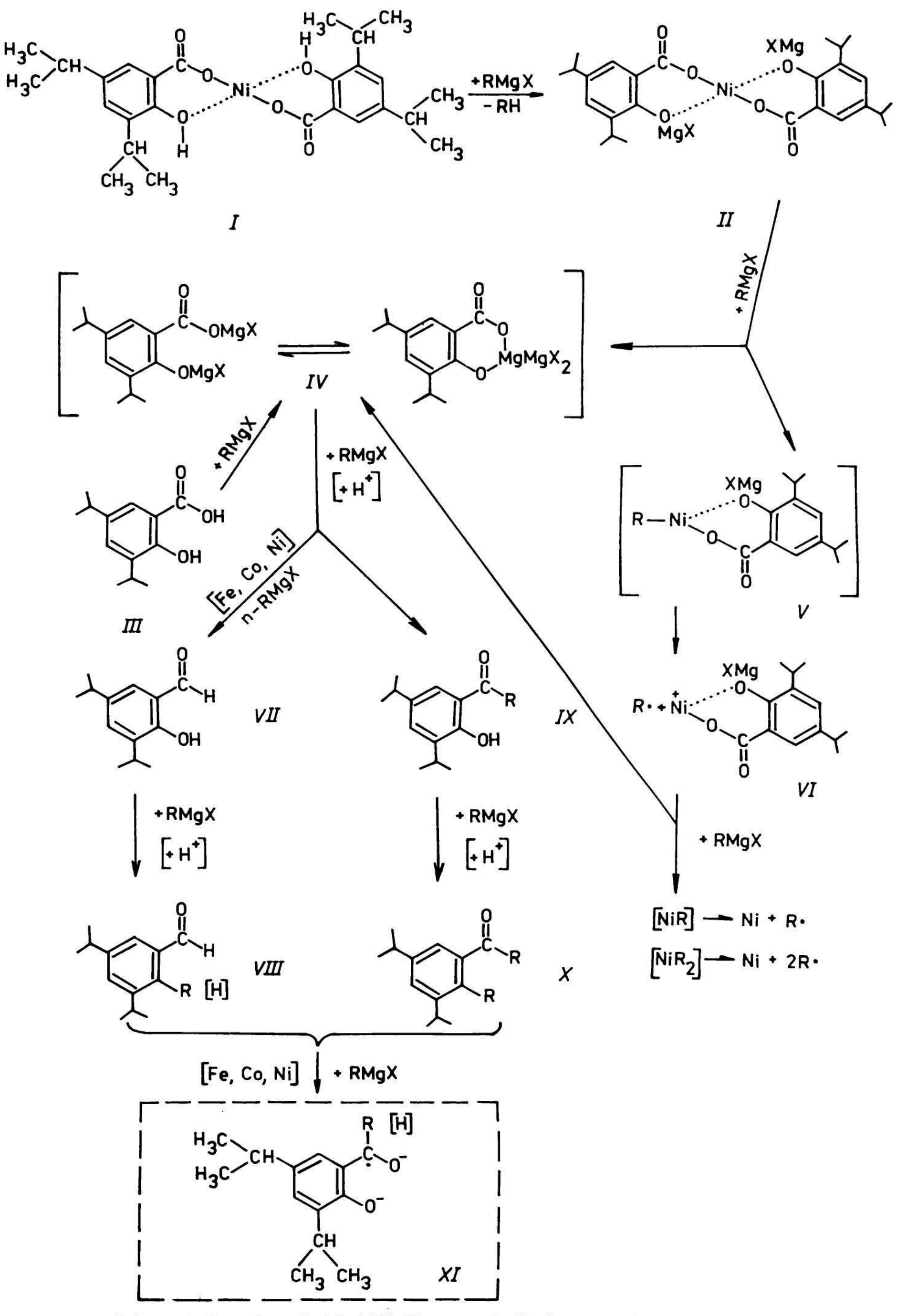
At the mole ratio Mg:Ni<4 the preferred reaction is that of RMgX with the hydrogen of the salicylic phenoxyl group with formation of product *II* and hydrocarbon RH. The diamagnetic compounds entering the reaction change to the paramagnetic products. From the high g_1 value 2.17 it is evident that the unpaired electron is localized on the transition metal. In the case of nickel e.s.r. is associated with the d^8 or d^9 configuration and the ferromagnetic resonance of nickel with d^{10} configuration. In view of the fact that at these mole ratios Mg:Ni the valence of nickel remains Ni(II) and the paramagnetic product behaves indifferently to the oxygen brought into the reaction mixture, the paramagnetism can be attributed to the d^8 configuration of nickel. The conversion of the diamagnetic compound *I* to the paramagnetic *II* can be explained as a consequence of the changes in the ligand field which are connected with the rearrangement of the d^8 electrons from the low to the high spin configuration.

By further reaction of compound *II* with RMgX the chelate ligand is transferred to magnesium and compound *IV* is formed (compound *IV* is also formed by the reaction of HDIPS (*III*) with RMgX); simultaneously, further alkylation of nickel takes place. The unstable Ni—C bond splits and the final product of the nickel alkylation is Ni(0). The singlet having $g_2=2.10$ was assigned to Ni(I), an intermediate product, which could be represented by the compound *VI*. The formation of Ni(I) as an intermediate between the two oxidation states of Ni(II) and Ni(0) is probable, because this paramagnetic product appears at a very advanced stage of the nickel reduction and, from the relatively high value of g_2, it is evident that the unpaired electron is localized on the transition metal. This paramagnetic product is destroyed in contact with oxygen or other oxidizing agents.

The products *VII*—*X* were identified in the reaction mixture and the formation of ketyl radicals *XI* with $g_3=2.004_2$ was confirmed in the systematic studies summarized below. The presence of transition metal (Fe, Co, Ni) is unavoidable to perform a successful generation of ketyl radicals.

2.2. Reduction of other nickel(II) chelates with various organometallic compounds

Another intensively investigated chelate ligand was nickel(II) acetylacetonate ($Niacac_2$) in the reaction with RMgX in etheric solutions [6]. At the mole ratios Mg:Ni<3 spectra characterized by a singlet having g values 2.05 were observed



Scheme 1. Reaction of nickel(II) diisopropylsalicylate with Grignard reagents

belonging to the reduced nickel (probably Ni(I)). At the ratio Mg : Ni = 3—4 anion radical of acetylacetonate was found. Employing organometallic compounds such as $AlEt_3$, n-BuLi in nonpolar solvents as toluene [7] and hexane [8] at lower ratios (Al, Li : Ni $<6:1$) formation of Ni(I) and at the higher ratios formation of radical with spectrum analogous to that of anion radical of acetylacetonate was observed. But the poorly resolved hyperfine structure of that spectrum includes also the alternative interpretation, the radical is the ligand acac with the abstracted methine hydrogen [7]. The addition of polar solvents like tetrahydrofuran (THF) to such systems at the ratios Mg, Li : Ni <4 results in the formation of Ni(II) high spin paramagnetic species.

Other nickel(II) compounds show a similar behaviour as described with $NiDIPS_2$ and $Niacac_2$. Generally, in the first stage of the reaction, at the lower ratios of organometallic compounds to nickel compounds, nickel remains in the valence state of Ni(II) in the low or high spin arrangement of its *d* electrons. The low spin arrangement is typical of nonpolar systems like *e.g.* $NiDIPS_2$ with $AlEt_3$ or n-BuLi in hexane solutions. The addition of benzene, THF or other more coordinative solvents than hexane, even in small amounts, stabilizes the high spin arrangement of Ni(II). This frequently reflects the catalytic properties of such systems. So *e.g.* is Ni(II) in a low spin state very effective in hydrogenations of olefins [8].

At the higher ratios of organometallic to nickel compounds (Al, Li : Ni) >3, mainly in the less polar solvents such as hexane, benzene, toluene, Ni(I) as an intermediate reduction product is observed. Stability of such species decreases in strongly polar solvents such as ethers, hexamethylphosphortriamide (HMPA), *etc.* Complex investigations of such systems were described in [7—10]. Ni(I) coordinated with monomer, placed on Ni(0) particles, was suggested to be active centre in the polymerization of butadiene [11].

The variation of chelate ligands, organometallic compounds, solvents, especially the addition of Lewis base or acid influences considerably the pathway of the reduction in such systems and this is frequently reflected in their catalytic properties. If the above-described reduction of $Niacac_2$ is carried out under the prior addition of BF_3OEt_2 to $Niacac_2$ this is rearranged forming $acacNiFBF_2acac$ or $NiF_2(BF_2acac)_2$ complexes, which are easily reduced under the formation of paramagnetic Ni(0) particles [7, 9, 10].

The third type of paramagnetic species frequently observed in such systems are anion radicals formed by the electron transfer to the chelate ligands, their reduction products or other substrates present in the system. The role of transition metal, structure and properties of such radical products were subject of our investigations and are summarized in the next parts of this contribution.

3. Ketyl radicals formed in the reactions of carboxylates with Grignard reagents

3.1. The structure of ketyl radicals formed from 3,5-diisopropylsalicylate ligand and alkyl from RMgX

Formation of stable ketyl radicals in the reaction of $NiDIPS_2$ with RMgX in the mole ratio Mg:Ni>6 was suggested in Scheme 1. The structure of the assumed ketyl radicals was determined by a systematic variation of the alkyl or aryl groups of the Grignard reagent and by the replacement of the nondeuterated groups by their deuterated counterparts [12].

In a similar reaction of $NiDIPS_2$ 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 [13]. On the other hand, in the reactions of Grignard reagents with a carbonyl group a transfer of one electron from the Grignard reagents to the carbonyl group [14—17] 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 radicals formed in agreement with Scheme 1.

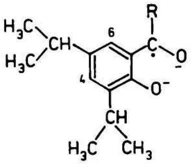
The reaction of $NiDIPS_2$ with different Grignard reagents, as well as with hydrides and n-BuLi, results in the formation of free radicals if the mole ratio Mg:chelate ligand>3. According to the type of Grignard reagents used the radical spectra observed can be divided into 6 groups; each with a characteristic e.s.r. spectrum:

1. *a*) $LiAlH_4$, $NaH_2[Al(OR)_2]$, LiH, n-BuLi; *b*) $LiAlD_4$.
2. *a*) CH_3MgI; *b*) CD_3MgI.
3. *a*) CH_3CH_2MgBr; *b*) CD_3CD_2MgBr.
4. [s-Pr—, s-Bu—]MgBr.
5. t-BuMgBr.
6. *a*) C_6H_5MgBr; *b*) C_6D_5MgBr.

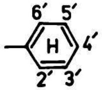
The splitting constants, obtained by the simulation of experimental spectra for each group, are summarized in Table 1. It is obvious that the radical structure depends on the type of Grignard reagent employed. Similar spectra were obtained with similar reagents, *e.g.* hydrides, n-alkyls and s-alkyls. 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. From these facts it was 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 of the reagents, we compared the spectra obtained in case when the nondeuterated reagents were replaced by their deuterated compounds.

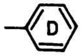
Table 1

Structure of radicals and the assignment of the splitting constants found by reactions of nickel(II) 3,5-diisopropylsalicylate with different Grignard reagents

Structure	R	Splitting constants, mT						
		a_3	a_4	a_5	a_6	$a_{1'}$	$a_{1''}$	$a_{2'-6'}$
	*1a*	0.06	0.59	0.06	0.42	1.39	—	—
	1b	0.06	0.59	0.06	0.42	0.214	—	—
	2a	0.069	0.51	0.069	0.45	1.265	—	—
	2b	0.069	0.51	0.069	0.45	0.194	—	—
	3a	0.071	0.5215	0.057	0.425	0.818	0.5465	—
	3b	0.071	0.5215	0.057	0.425	0.1256	0.0836	—
	4	0.05	0.479	0.05	0.407	0.3	—	—
	5	Formation of radicals was not observed						
	6a	<0.05	0.135	<0.05	0.135	$a_{2'}$ 0.414 $a_{3'} = a_{5'}$ 0.135 $a_{4'}$ 0.523 $a_{6'}$ 0.438		
	6b	Nonresolved spectrum				$(C_6D_5 \underset{D}{\overset{H}{\rightleftharpoons}} C_6D_xH_y)MgBr$; $x + y = 5$		

R: *1a*) $\overset{1'}{-H}$; *1b*) $\overset{1'}{-D}$; *2a*) $\overset{1'}{-CH_3}$; *2b*) $\overset{1'}{-CD_3}$; *3a*) $\overset{1'}{-CH_2}CH_3$; *3b*) $\overset{1'}{-CD_2}CD_3$; *4*) $\overset{1'}{-CH}(CH_3)_2$; *5*) $\overset{1'}{-C}(CH_3)_3$;

6a) 

; *6b*) 

The simplest situation would be expected with hydrides, *i.e.* in group *1*, where only simple atom such as hydrogen or deuterium can be transferred from the reduction reagent to the chelate ligand. Spectrum *1a*, corresponding to the application of $LiAlH_4$, was simulated by means of the following splitting constants of protons: $a = 1.39$ mT, $a = 0.59$ mT, $a = 0.42$ mT, and $2 \times a = 0.06$ mT. The two constants having $a = 0.06$ mT were not evident from the spectrum measured at the given resolution, but we specified them here, as splitting constants of this order were found with reagents of groups *2* and *3*. Using $LiAlD_4$ instead of $LiAlH_4$ the obtained spectrum was simulated by means of the parameters of the nondeuterated compound *1a* but one splitting constant for a proton having $a = 1.39$ mT was exchanged with the corresponding parameter for deuteron ($a = 0.214$ mT). 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 splitting constant for the proton originating from hydride deserves attention.

The spectrum obtained for group *2a*, employing CH_3MgI, was simulated using splitting constants of four protons having similar values as found for the chelate ligand in group *1* ($a = 0.51$ mT; $a = 0.45$ mT; $2 \times a = 0.06$ mT), and furthermore with splitting constants of three equivalent protons having $a = 1.265$ mT, believed to originate from the methyl group. This is confirmed by spectrum *2b* measured replacing CH_3MgI by CD_3MgI. The deuterated radical was described using parameters of the nondeuterated compound *2a*, exchanging the splitting constant of three protons ($a = 1.265$ mT) with the corresponding constant of deuterons ($a = 0.194$ mT).

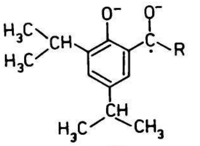
In group *3a* the spectrum of the nondeuterated radical was simulated again using splitting constants of four protons ($a = 0.5215$ mT; $a = 0.425$ mT; $a = 0.071$ mT; $a = 0.057$ mT) having similar values to those assigned to the chelate protons in group *1* and *2* and, furthermore, with splitting constants of two protons having $a = 0.818$ mT and $a = 0.5465$ mT. Analogously to groups *1* and *2*, we assigned these two constants to the protons originating from the ethyl group. This assignment is confirmed by structure *3b* obtained using C_2D_5MgBr instead of C_2H_5MgBr. Spectrum *3b* was simulated using the parameters for *3a* replacing the splitting constants of two protons ($a = 0.818$ mT and $a = 0.5565$ mT) by the corresponding splitting constants of deuterons ($a = 0.1256$ mT and $a = 0.0836$ mT). From these results it is obvious that these two protons originate from ethyl group. A remarkable feature is their lack of equivalence which is probably caused by the hindered rotation of the alkyl moiety.

The spectra measured by application of s-alkyl MgBr were described employing three splitting constants ($a = 0.479$ mT, $a = 0.407$ mT, and $a = 0.3$ mT). Analogously to the results in the groups *1, 2,* and *3*, $a = 0.3$ mT was assigned to the proton of the s-alkyl group (≧C—H) and the remaining two splitting constants

($a = 0.479$ mT and $a = 0.407$ mT) to the protons of the salicylate ligand. In group *5,* using t-BuMgBr, no formation of radicals was observed.

In group *6,* using nondeuterated PhMgBr the obtained spectrum was described by splitting constants $a = 0.523$ mT, $a = 0.438$ mT, $a = 0.414$ mT, $4 \times a = 0.135$ mT, and $2 \times a = 0.05$ mT. With experiment *6b* using the deuterated phenyl compound the expected information was not obtained as exchange between the deuterons and the protons of the phenyl group took place; therefore the resulting nonresolved spectrum *6b* is the sum of the differently deuterated radical spectra. Spectrum *6b* is narrower than *6a*. This indicates that the protons of the phenyl group participate in the formation of radical structure. The assignment of the splitting constants to the protons in the phenyl group and to the protons in the salicylic group, as given in Table 1, is based on a common structure and further results discussed below.

On the basis of the structure of the products formed during the reaction and the described analysis of e.s.r. spectra, the observed radicals can be characterized by the common structure *XI* formulated in Scheme 1. The below summarized investigations on various salicylate ligands bring its further confirmation.



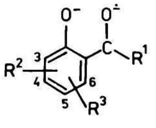
XI

(R = H, alkyl, Ph)

3.2. $^{-}$O—Ar—CO$^{\dot{-}}$—R *radicals from* HO—Ar—COOH *and* RMgX

Previous systematic study of $NiDIPS_2$ with RMgX under variation of R was extended to the variously substituted salicylic acids. The following acids, 2-hydroxybenzenecarboxylic acid (*XII*) and its substituted homologues 5-t-butyl (*XIII*), 3,5-di-t-butyl (*XIV*), 3,5-di-i-propyl (*XV*), 4-methyl (*XVI*), 4-ethyl (*XVII*), 4-i-propyl (*XVIII*), 4-t-butyl (*XIX*) were exploited in the reactions with the following Grignard reagents, CH_3MgBr (*a*), C_2H_5MgBr (*b*), C_2D_5MgBr (*c*), and n-C_3H_7MgBr (*d*) under the conditions as described in [18].

The obtained radicals can be characterized by the common structure.



XII—XIXa—d

R^1 = CH_3, C_2H_5, C_2D_5, n-C_3H_7

R^2, R^3 = CH_3, C_2H_5, i-C_3H_7, t-C_4H_9

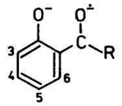
As in the previous group of radicals, here again, the hydrogen of the phenoxy group is eliminated to give oxido anion and carboxylic group is reduced to carbonyl. Transition metal present in the system enables the formation of ketyl radicals. The splitting constants obtained by the simulation of experimental spectra of corresponding structures *XII—XIXa—d* are summarized in Table 2. Their assignment to the R^1 alkyl protons is based on a similar procedure as described above in 3.1. and in more detail in [18]. There remained to assign the splitting constants of the structures *XII—XIX* with the average values $\bar{a}_3 = 0.125$ mT, $\bar{a}_4 = 0.53$ mT, $\bar{a}_5 = 0.16$ mT, and $\bar{a}_6 = 0.45$ mT to the individual protons of the benzene ring. In accord with the known distribution of spin density of the unpaired electron in aryl ketyl radicals the highest splitting constant a_4 is due to the *para* proton, the second highest a_6 to the *ortho* proton, and the ramaining a_3 and a_5 are due to the *meta* protons in phenyl group. Such assignment of the splitting constant a_4 follows also from structure *XIX*, where substitution of the *para* proton by t-butyl group causes the interaction corresponding to the absence of $\bar{a}_4 = 0.53$ mT in the spectrum, whereas the other constants have approximately the original values. Assignment of the *meta* protons was explained similarly with the structure *XIII* in which the 5-proton is replaced by t-butyl group, and, consequently, the spectrum lacks the splitting constant a_5. Changes of splitting constants of the remaining structures agree with this assignment. Thus *e.g.* substitution of the 4-proton by CH_3, C_2H_5, i-C_3H_7, t-C_4H_9 (structures *XVI—XIX*) causes a gradual lowering (in the case of t-C_4H_9 disappearance) of the splitting constant at position 4. Similarly, due to substitution of the 3,5-protons by t-C_4H_9 (structure *XIV*) the splitting constants a_3 and a_5 are absent in the spectrum.

Considering the influence of substituents on distribution of the unpaired electron spin density, the comparison of the splitting constants a_3, a_4, a_5, a_6 of the benzene ring protons for a single acid (*e.g.* the structure *XIIa—d*) in Table 2 indicates that their values are practically independent of the alkyls in the Grignard reagents *a—d*. Therefore, for further discussion Table 3 gives average values of the splitting constants $\bar{a}_4$, $\bar{a}_6$ of the structures *a—d* for the respective structures *XII—XIX*. The effect of the alkyl substituents will be obtained from the comparison of the nonsubstituted structure *XII* with the splitting constants of *XIII—XIX*.

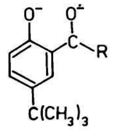
From data in Table 3 it follows that the gradual substitution of benzene ring at 3,5 positions (structures *XII—XV*) results in decrease of splitting constants at position 4 and 6. This decrease is relatively small but, within the experimental error, statistically significant. Small increase of splitting constant a_6 is encountered with the structures *XVI—XIX* as compared with *XII* due to alkyl substitution at position 4. This increase is, however, insignificant. The effect of alkyl substituents R^2, R^3 in the benzene ring on the splitting constants $a_{1'}$ and $a_{1''}$ of the alkyl protons in β position of the ketyl is insignificant, too. The constants $a_{1'}$ and $a_{1''}$ of structures *XVI*, *XVII* are very close to those of *XII*. Substitution in the structures *XIV*, *XV*

Table 2

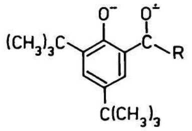
Structures and assignment of splitting constants of ketyl radicals generated by reactions of alkyl-substituted 2-hydroxybenzenecarboxylic acids with alkylmagnesium halogenides



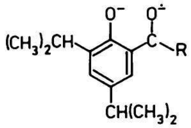
XIIa—d



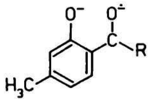
XIIIa—d



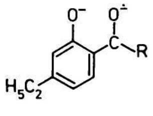
XIVa—d



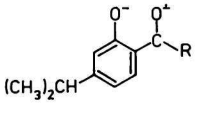
XVa—d



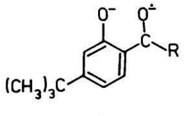
XVIa—d



XVIIa—d

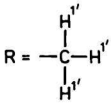


XVIIIa—d

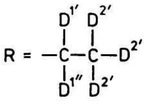


XIXa—d

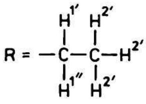
a)



c)



b)



d)

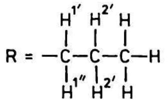
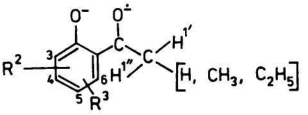


Table 2 (Continued)

Structures		Splitting constants, mT						
		a_3	$a_{4(\alpha)}$	a_5	a_6	$a_{1'}$	$a_{1''}$	$a_{2'}$
XII	*a*	0.12	0.571	0.16	0.469	1.24	—	—
	b	0.12	0.571	0.16	0.469	0.676	0.598	—
	c	0.12	0.571	0.16	0.469	0.098	0.0866	—
	d	0.125	0.561	0.155	0.469	0.686	0.598	0.062
XIII	*a*	0.117	0.568	—	0.459	1.24	—	—
	b	0.117	0.568	—	0.459	0.658	0.568	—
	c	0.117	0.568	—	0.459	0.1005	0.0875	—
	d	0.117	0.568	—	0.459	0.658	0.568	0.058
XIV	*a*	—	0.532	—	0.435	1.235	—	—
	b	—	0.53	—	0.43	1.205	0.38	—
	c	—	0.532	—	0.4315	0.1815	0.0565	—
	d	—	0.519	—	0.439	1.228	0.303	0.073
XV	*a*	0.069	0.52	0.069	0.42	1.265	—	—
	b	0.057	0.5215	0.071	0.425	0.818	0.5465	—
	c	0.057	0.5215	0.071	0.425	0.1256	0.0836	—
	d	0.064	0.525	0.064	0.428	0.828	0.575	0.064
XVI	*a*	0.125	0.591	0.154	0.484	1.25	—	—
	b	0.134	0.591	0.154	0.484	0.684	0.617	—
	c	0.123	0.591	0.154	0.484	0.1073	0.089	—
	d	0.116	0.60	0.153	0.493	0.652	0.63	0.06
XVII	*a*	0.13	0.46	0.16	0.491	1.26	—	—
	b	0.13	0.452	0.16	0.491	0.68	0.60	—
	c	0.13	0.452	0.16	0.491	0.1025	0.0905	—
	d	0.122	0.457	0.158	0.477	0.77	0.535	0.055
XVIII	*a*	0.13	0.285	0.155	0.495	1.25	—	—
	b	0.13	0.287	0.155	0.492	0.685	0.607	—
	c	0.132	0.27	0.157	0.480	0.107	0.093	—
	d	0.13	0.287	0.155	0.492	0.685	0.607	0.064
XIX	*a*	0.13	—	0.16	0.48	1.27	—	—
	b	0.13	—	0.155	0.492	0.685	0.607	—
	c	0.13	—	0.155	0.50	0.106	0.09	—
	d	0.122	—	0.165	0.484	0.664	0.632	0.063

Table 3

Experimental values of splitting constants of protons found for various substitutions of benzene ring in ketyl radicals



Compound	R^2, R^3	Splitting constants, mT			
		$\bar{a}_4$ [a]	$\bar{a}_6$ [a]	$a_{1'}$ [b]	$a_{1''}$ [b]
XII	unsubstituted	0.569	0.469	0.681	0.598
XIII	5-t-C_4H_9	0.568	0.459	0.658	0.568
XIV	3,5-di-t-C_4H_9	0.528	0.434	1.216	0.341
XV	3,5-di-i-C_3H_7	0.522	0.424	0.823	0.567
XVI	4-CH_3	—	0.486	0.668	0.624
XVII	4-C_2H_5	—	0.488	0.725	0.567
XVIII	4-i-C_3H_7	—	0.490	0.685	0.607
XIX	4-t-C_4H_9	—	0.489	0.675	0.619

a) Average values of the splitting constants of the structures *a*—*d*;
b) average values of the splitting constants of the structures *b*, *d*.

causes an increase of nonequivalence of the protons 1′ and 1″, but their overall spin density is not markedly increased when compared with the respective protons of *XII*.

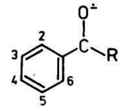
Generally, alkyl substituents in benzene ring and in alkyl group of the discussed radical type do not affect the spin density distribution of the unpaired electron. This remarkable fact can be logically explained, if the oxido anion group at position 2 and its strong electron-donor effect are taken into account. The push effect of this group is so marked that relative contributions of alkyl groups are small and practically nondetectable in the spectrum. This explanation is supported by further experiments and INDO calculations which were carried out with similar structures, but without the oxido anion group, and are described below.

3.3. Ar—$CO^{\dot{-}}$—R *radicals from* ArCOOH *and* RMgX

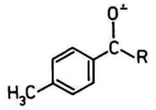
Reactions of R^1-substituted benzenecarboxylic acids (R^1 = H, Me, Et, and t-Bu) with R^2MgX (R^2 = Et and n-Pr) in the presence of nickel produce ketyl radicals R^1—Ar—$CO^{\dot{-}}$—R^2 [19]. The splitting constants obtained by the simulation of the experimental spectra (structures *XX*—*XXIV*) are summarized in Table 4. Their assignment for *XXb* is based on our previous studies and on the deuteration experiments.

Table 4

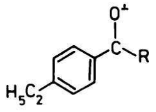
Assignment of the splitting constants of the protons to the radical structures *XX—XXIVa—c*



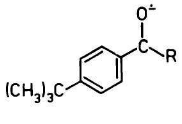
XXb



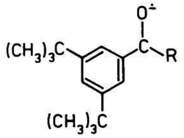
XXIa, b



XXIIa, b

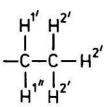


XXIIIa, b



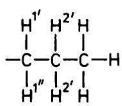
XXIVa—c

a) R =



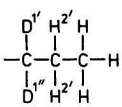
$-\overset{H^{1'}}{\underset{H^{1''}}{C}}-\overset{H^{2'}}{\underset{H^{2'}}{C}}-H^{2'}$

b) R =



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

c) R =



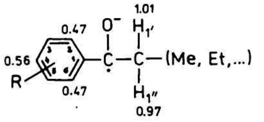
$-\overset{D^{1'}}{\underset{D^{1''}}{C}}-\overset{H^{2'}}{\underset{H^{2'}}{C}}-\overset{H}{\underset{H}{C}}-H$

Structures		Splitting constants, mT							
		a_2	a_3	a_4	a_5	a_6	$a_{1'}$	$a_{1''}$	$a_{2'}$
XX	*a*	Little stable radical							
	b	0.47	0.12	0.52	0.12	0.47	1.02	0.92	—
XXI	*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
XXII	*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
XXIII	*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	—
XXIV	*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	—

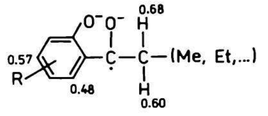
The two highest values of splitting constants were assigned to the protons of alkyl at β position of ketyl group, the next highest value was assigned to *para* position, the next two ones to *ortho* position of benzene ring. This assignment was confirmed by the structures *XXI—XXIV* showing the expected magnitude change of splitting constants and change in number of hyperfine splittings in the e.s.r. spectra in accordance with the change of substituents.

In the case of the well-resolved spectra of structures *XXIb* and *XXIIb* an indication of hyperfine splitting with the splitting constant $a_2 \doteq 0.04$ mT was observed. On the basis of an analogous finding described in 3.2. the interactions were assigned to the γ protons of ketyl group with the unpaired electron. In analogy to aryl alkyl ketyl radicals (3.2.) the nonequivalence of β hydrogen atoms is observed also here, which is probably connected with the hindered rotation of the alkyl group.

From Table 4 it follows that the influence of the investigated alkyl groups on distribution of the unpaired electron density is negligible. In this context it is interesting to compare the investigated alkyl phenyl ketyl radicals without oxido anion group with the above-described 2-oxido anion phenyl alkyl ketyl radicals. These two types of radicals can be characterized by the following structures and average numerical values of splitting constants marked at the corresponding positions of the individual protons.



XX-XXIV



XII-XIX

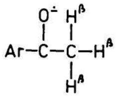
Striking is the effect of oxido anion group which, on going from structures *XX—XXIV* (without oxido anion) to structures *XII—XIX* (with oxido anion) manifests itself by lowering of values of the splitting constants of the β protons of ketyl group ($a_{1'}^{XX-XXIV} = 1.01$ mT $\rightarrow$ $a_{1'}^{XII-XIX} = 0.68$ mT and $a_{1''}^{XX-XXIV} = 0.97$ mT $\rightarrow$ $a_{1''}^{XII-XIX} = 0.60$ mT). This effect can be explained by the extended delocalization of the unpaired electron towards the oxido anion group, which results in a decreased $\sigma - \pi$ polarization and consequently decreased values of the splitting constants of β protons in structures *XII—XIX*.

3.4. Nonequivalence of β and interaction of γ protons of ketyl group with unpaired electron

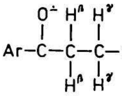
Interaction of γ protons

The investigated series of radicals *XII—XIX*, *XX—XXIV* as well as radicals described in [20] can, with respect to β and γ protons of the ketyl group, be characterized generally by the structures

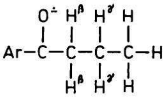
XII-XIX, XX-XXIV

i) 

$\mathrm{Ar{-}\overset{O^{\dot{-}}}{C}{-}\overset{H^{\beta}}{\underset{H^{\beta}}{C}}{-}H^{\beta}}$

ii) 

$\mathrm{Ar{-}\overset{O^{\dot{-}}}{C}{-}\overset{H^{\beta}}{\underset{H^{\beta}}{C}}{-}\overset{H^{\gamma}}{\underset{H^{\gamma}}{C}}{-}H^{\gamma}}$

iii) 

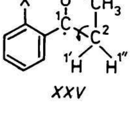
$\mathrm{Ar{-}\overset{O^{\dot{-}}}{C}{-}\overset{H^{\beta}}{\underset{H^{\beta}}{C}}{-}\overset{H^{\gamma}}{\underset{H^{\gamma}}{C}}{-}\overset{H}{\underset{H}{C}}{-}H}$

where Ar represents the aromatic ring of the benzenecarboxylic acids. It is noteworthy to compare interactions of the individual protons at β and γ positions of the ketyl group with the unpaired electron. If there is a methyl group at that position (type i)), its protons are equivalent with the splitting constant 1.25 mT. On the contrary, if there are methylene protons at position of ethyl group (type ii)), their nonequivalence is manifested in the values of the splitting constants 0.6 and 0.7 mT, which indicates limited rotation of methylene group. Interaction of the *γ* protons (*i.e.* methyl protons) of the ethyl group is not manifested in the spectrum. In the third case (type iii)) the respective alkyl is n-propyl. The *β* protons usually have the same values of the splitting constants as those in ethyl group. At γ position there are not methyl but methylene protons (in contrast to the type ii)). It is remarkable that the substitution of methyl by methylene protons at γ position is manifested by interaction of the methylene protons with the unpaired electron, the splitting constant being 0.07 mT. Analogous phenomenon was observed for longer n-alkyl group, too. This effect is less expressive by structures *XX—XXIV* than by *XII—XIX*.

Interactions of *γ* protons are rare and their mechanism of transfer of spin density of the unpaired electron is not clear. Furthermore, in the studied system different behaviour of methyl and methylene protons at γ position is observed. Obviously the methyl group rotates freely in contrast to the methylene group the rotation of which will probably be limited, its sterical orientation towards the ketyl group being possible. The observed splitting of the *γ* protons could be explained by hyperconjugation mechanism.

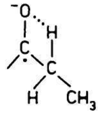
Nonequivalence of *β* protons

The nonequivalence of *β* protons was studied by INDO calculations [21] exploiting a model structure

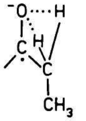


XXV

According to the optimalization of various counter ions of ketyl radicals the best agreement between experiment and simulation for the radicals *XII—XIXb—d* ($X=O^-$) was obtained if $M=NiCl_2$ and for radicals *XX—XXIV* ($X=H$) if $M=NiCl_3^-$. The minima of the calculated total energy at various dihedral angles φ marked by atoms $OC^1C^2C^3$ were obtained for $\varphi=120°$ and $\varphi=240°$. Rotation barrier was calculated to be 40—50 kJ mol^{-1} suggesting a strong hindrance in the rotation of methylene group in two positions as given by structures



XXVIa



XXVIb

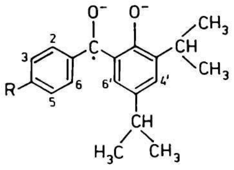
The total energy of structure *XXVIb* is about 5 kJ mol^{-1} higher than that of *XXVIa*. This suggests that the configuration *XXVIa* is the mostly populated one. The calculated values of the splitting constants of *XXVIa* are in good agreement with experiment and confirm the hindered rotation of methylene group in the plane of aromatic ring involving the interaction of the methylene hydrogens with the oxygen of the ketyl group. More details on these investigations are given in [21].

3.5. (Ar—, $^-$O—Ar—)CO$^{\dot{-}}$—Ar *radicals from* ArCOOH, HO—ArCOOH, *and* ArMgX

In the reactions of alkyl-substituted-benzenecarboxylic acids and -2-hydroxybenzenecarboxylic acids (ArCOOH and HOArCOOH) with alkyl-substituted phenyl Grignard reagents (ArMgX) in the presence of nickel, ketyl radicals (Ar—, $^-$O—Ar—)CO$^{\dot{-}}$—Ar are formed [22]. Splitting constants obtained by the simulation of experimental e.s.r. spectra observed in the reactions of 2-hydroxy-3,5-diisopropylbenzenecarboxylic acid with 4-R-substituted phenylmagnesium bromides are given in Table 5. The systematic change of the substituent R (H—, Me—, Et—, i-Pr—, and t-Bu—) is reflected in the hyperfine structure of the spectra. Thus, on replacing the proton in position 4 ($a_4=0.519$ mT) (*XXVIIa*) by methyl group (*XXVIIb*) the interaction of the unpaired electron with three equivalent protons ($a_4=0.548$ mT) is observable, whereas the remaining splitting constants are unchanged (Table 5). Similarly, on replacing the proton in position 4 by ethyl, i-propyl or t-butyl group (*XXVIIc—e*) the expected changes in the values of splitting constants and the number of splittings were observed. This suggests that the spin density of the unpaired electron on the 4-alkyl-substituted phenyl ring is considerably higher than the density on the ring with the oxido anion group.

Table 5

Change of nonequivalence of the *ortho* protons (a_2, a_6) with substituent R in 1-(4-R-phenyl)-1-[2-oxido-3,5-diisopropyl]phenyl ketyl radicals

Structures		Splitting constants, mT							
		a_2	a_3	a_4	$a_{4\alpha}$	a_5	a_6	$a_{4'}$	$a_{6'}$
 *XXVII*	*a*	0.43	0.145	0.519	—	0.145	0.422	0.115	0.115
	b	0.43	0.145	—	0.548	0.145	0.42	0.115	0.115
	c	0.43	0.135	—	0.41	0.135	0.40	0.115	0.115
	d	0.435	0.135	—	0.23	0.135	0.395	0.117	0.117
	e	0.435	0.137	—	—	0.137	0.395	0.115	0.115

R: *a*) —H; *b*) $-\mathrm{C\overset{\alpha}{H}_3}$; *c*) $-\mathrm{C\overset{\alpha}{H}_2CH_3}$; *d*) $-\mathrm{C\overset{\alpha}{H}(CH_3)_2}$; *e*) $-\mathrm{C(CH_3)_3}$.

Therefore, the other two splitting constants with the higher values were assigned to positions 2 and 6 ($a_2 \doteq 0.43$ mT; $a_6 \doteq 0.41$ mT). The remaining two pairs of splitting constants were assigned as follows: $a_3 = a_5 \doteq 0.14$ mT and $a_{4'} = a_{6'} \doteq 0.115$ mT [22].

A remarkable feature of structures *XXVIIa—e* is the increase in the nonequivalence of the protons in position 2 and 6 with the increasing size of the R substituent in position 4. This points to the hindered rotation of this phenyl group, which may be caused by the steric hindrance of the substituents or by their inductive effect; this effect increases the bond order between the phenyl ring and ketyl group and consequently slows down the rotation.

The second group of ketyl radicals *XXVIII—XXXI* (Table 6) is represented by the alkyl-substituted aryl aryl ketyl radicals. Structures *XXVIII—XXX* show the push effect of a methyl (*XXIX*) and a 4-t-butyl (*XXX*) group on the unpaired density. The methyl and t-butyl groups decrease the unpaired spin density in the *ortho* and *para* position of the substituted ring by about 3 % (*XXIX*) and 6 % (*XXX*) and increase this in the same way on the other ring ($a_{2'}$, $a_{4'}$, $a_{6'}$). Substitution in the 3',5'-position with two methyl groups (*XXXI*) reduces the push effect of the t-butyl group described for *XXX*.

The third group of radicals (*XXXII—XXXV*; Table 7) illustrates the effect of the oxido anion group on the distribution of unpaired spin density. Two pairs of radicals (*XXXII*, *XXXIII* and *XXXIV*, *XXXV*) with similar structures differ only in the presence of the oxido anion group substituted in position 2. On comparing *XXXII* with *XXXIII* (without and with the oxido anion group) a decrease of the splitting constants of the oxido anion substituted ring is observed, *e.g.* $a_4^{XXXII} = 0.282$ mT → $a_4^{XXXIII} = 0.25$ mT or $a_6^{XXXII} = 0.255$ mT → $a_6^{XXXIII} = 0.21$ mT. Simul-

Table 6

Influence of alkyl substituents (Me—, t-Bu—) on the proton splitting constants of diphenyl ketyl radicals

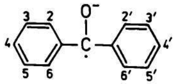
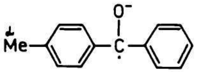
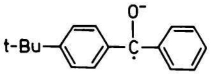
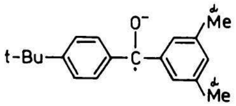
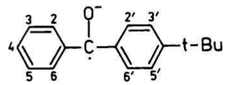
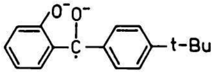
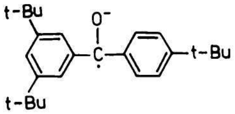
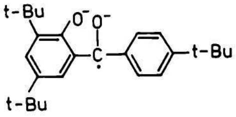
Structures		Splitting constants, mT									
		a_2	a_3	$a_{4,4\alpha}$	a_5	a_6	$a_{2'}$	$a_{3',3'\alpha}$	$a_{4'}$	$a_{5',5'\alpha}$	$a_{6'}$
XXVIII		0.29	0.102	0.358	0.102	0.29	0.29	0.102	0.358	0.102	0.29
XXIX		0.28	0.104	0.346	0.104	0.28	0.30	0.104	0.374	0.104	0.30
XXX		0.271	0.103	—	0.103	0.271	0.306	0.103	0.383	0.103	0.306
XXXI		0.275	0.105	—	0.105	0.275	0.295	0.095	0.36	0.095	0.295

Table 7

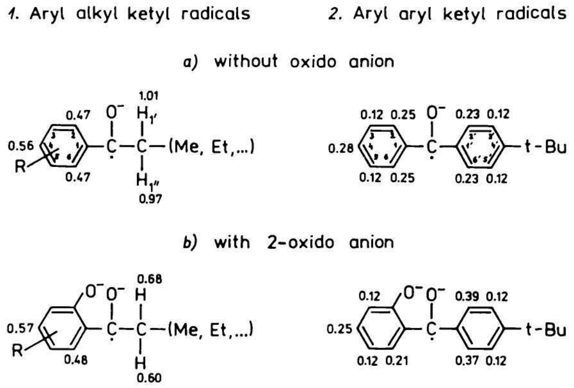
Two pairs of structures (*XXXII, XXXIII, XXXIV, XXXV*) showing the influence of the oxido anion group on the proton splitting constants of diphenyl ketyl radicals

Structures	Splitting constants, mT									
	a_2	a_3	a_4	a_5	a_6	$a_{2'}$	$a_{3'}$	$a_{4'}$	$a_{5'}$	$a_{6'}$
XXXII 	0.255	0.125	0.282	0.125	0.255	0.228	0.125	—	0.125	0.228
XXXIII 	—	0.10	0.25	0.10	0.21	0.395	0.12	—	0.12	0.37
XXXIV 	0.23	—	0.25	—	0.23	0.28	0.13	—	0.13	0.27
XXXV 	—	—	0.115	—	0.115	0.45	0.14	—	0.14	0.415

taneously, the push effect of the oxido anion group leads to a near doubling of the unpaired spin density on the other phenyl ring; $a_{2'}^{XXXII}=0.228$ mT → $a_{2'}^{XXXIII}=$ 0.395 mT and $a_{6'}^{XXXII}=0.228$ mT → $a_{6'}^{XXXIII}=0.37$ mT. A similar situation arises in *XXXIV* and *XXXV* (Table 7). Thus, the 2-oxido anion substituent represents a group with one of the strongest push effects on aryl aryl ketyl radicals so far observed.

3.6. Oxido anion group and its push and pull effect on the distribution of unpaired electron density

The investigated ketyl radicals, according to their structure and the influence of the substituents on the distribution of unpaired electron, can be divided into the following groups



The numbers marked at the individual proton positions represent numerical values of their splitting constants expressed in mT. The first group (*1,2*)*a* differs from the second one (*1,2*)*b* by oxido anion group in position 2 of the phenyl ring.

When compared aryl alkyl ketyl radicals of type *1a* with *1b*, remarkable is the decrease of splitting constants of β protons ($a_{1'}=1.01$ mT and $a_{1''}=0.97$ mT by structure *1a* decrease to $a_{1'}=0.68$ mT and $a_{1''}=0.60$ mT by structure *1b*). An opposite effect shows the oxido anion group by the couple of radicals *2*(*a*,*b*) where by the substitution with oxido anion group the unpaired spin density on the unsubstituted benzene ring increases nearly by factor two ($a_{2',6'}=0.25$ mT by structure *2a* increases to $a_{2'}=0.39$ mT and $a_{6'}=0.37$ mT by structure *2b*).

This, apparently, contradictory (push and pull) effect of the oxido anion group can be explained by its dual (electron-donor and electron-acceptor) ability. In aryl alkyl ketyl radicals *1*(*a*,*b*) alkyl groups (Me, Et) themselves are strongly donating substituents showing a considerable push effect. So the oxido anion group functions here as electron-accepting substituent, widens the conjugation of aromatic system and enables the delocalization of unpaired electron on its oxygen atom. Therefore the σ—π polarization and herewith the spin density and splitting constants of protons in the alkyls attached to the ketyl group decrease by oxido anion substituted radicals as it is obvious from the comparison of structures *1a* and *1b*.

An opposite effect, comparing to that of radicals *1*(*a*,*b*), shows the oxido anion group by the couple of radicals *2*(*a*,*b*). Here, instead of alkyl groups (Me, Et...) in the radicals *1*(*a*,*b*), the aromatic ring is possessing electron-acceptor properties. It widens the conjugation and enables the delocalization of unpaired electron in its π orbitals. Herewith dominate here the electron-donor properties of oxido anion group very expressively. The unpaired spin density and consequently the splitting constants of protons of the unsubstituted phenyl ring are increased considerably as it can be seen from the comparison of structure *2a* to *2b*.

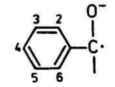
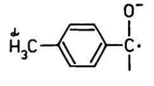
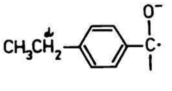
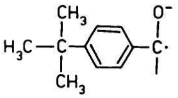
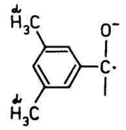
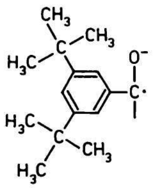
The shape of molecular orbitals containing one electron, at least in the first approximation, obtained by INDO calculations [21] confirms the experimentally observed distribution of unpaired electron. In the case of radical type *1*(*a*,*b*) the oxido anion group substituted in position 2 of the aromatic ring enables an increase of the delocalization of unpaired electron on the substituted oxygen atom. Otherwise the substitution of oxido anion group in radical type *2*(*a*,*b*) results in the decrease of spin density on the substituted benzene ring. A considerable transfer of electron density to the oxygen, caused by the polarization of the lower with two electrons occupied molecular orbitals, is then mainly compensated by the transfer of spin density to another aromatic ring. So a remarkable increase of proton splitting constants in positions 2′ and 6′ is observable when comparing structure *2a* with *2b*.

4. Anion radicals of carboxylates

In the reactions of *meta* and *para* alkyl-substituted benzoic acids with aryl Grignard reagents, in tetrahydrofuran solutions and in the presence of nickel salts, the e.s.r. spectra of the anion radicals of carboxylates derived from the benzoic acids which represent the intermediates in the formation of ketyl radicals were observed [23]. The structure of the observed radicals depends on the benzoic acid substituents but is independent of the Grignard reagents (C_6H_5—, C_6D_5—, 4-t-Bu—C_6H_4—, and 4-Me—C_6H_4—)MgBr. From the analysis of the spectra it is obvious that the unpaired electron spin density is distributed on the benzene ring originating from the benzoic acids, and no interaction of the unpaired electron with the protons originating from the Grignard reagents is observable. Splitting constants found by the simulation of experimental spectra (Table 8) are assigned in accord with the generally known distribution of unpaired electron in aromatic systems. When comparing structure *XXXVI* with *XXXVII—XLI* the substituted derivatives of *XXXVI* justify such an assignment. On replacing the proton of benzoic acid in *para* position by methyl group (*XXXVII*) splittings from three equivalent protons in the 4-α position were found; analogously, on replacing the proton by an ethyl group (*XXXVIII*) splittings from two equivalent protons were given and no splittings are observable for the 4-α substituents in the e.s.r. spectra of the t-butyl derivative (*XXXIX*). Similarly, on the substitution of *meta* protons by methyl groups (*XL*) and t-butyl groups (*XLI*) corresponding changes in the hyperfine structure of the spectra were observed (Table 8). This suggests that the

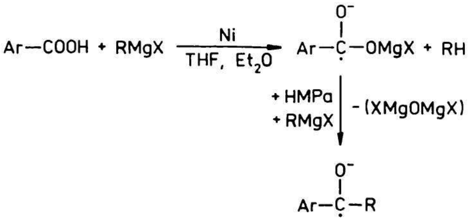
Table 8

Structures of the anion radicals of carboxylates observed in the reactions of alkyl-substituted benzoic acids with aryl Grignard reagents, and the assignment of their proton splitting constants

Structures		Splitting constants, mT				
		a_2	$a_{3,3\alpha}$	$a_{4,4\alpha}$	$a_{5,5\alpha}$	a_6
XXXVI		0.45	0.145	0.55	0.145	0.435
XXXVII		0.454	0.153	0.568	0.153	0.434
XXXVIII		0.42	0.155	0.44	0.155	0.42
XXXIX		0.451	0.132	—	0.132	0.451
XL		0.445	0.145	0.53	0.145	0.425
XLI		0.44	—	0.49	—	0.44

basic structure of these radicals originates from the benzoic acid and that the unpaired spin density is centred on its carbonyl group. The alternative, where phenyl group R, originating from the Grignard reagents RMgX, is also bonded directly to the carbonyl group but is not coplanar with the benzoic acid Ar ring, is not probable as the very well resolved e.s.r. spectrum of *XXXVI*, with peak-to-peak width of 0.035 mT, does not show the interaction of protons originating from R with the unpaired electron.

Anion radicals of carboxylates are formed in the primary stage of the reaction as, after addition of hexamethylphosphortriamide (HMPA), they are converted to ketyl radicals having splitting constants similar to those described in Part 3. The following reaction scheme is suggested for the formation of the anion radicals of the carboxylates, Ar—CO$^{\dot{-}}$—OMgX.



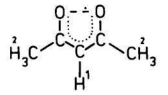
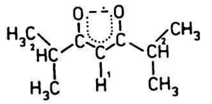
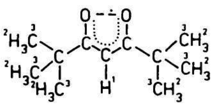
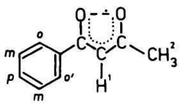
In the reactions of Grignard reagents with carboxylic acids, tertiary alcohols are usually obtained without any intermediate products, as the successive reaction of Grignard reagents proceeds very quickly. In Part 3 it was reported on the ability of nickel to stabilize the intermediate keto products in the form of their ketyl radicals. Analogously here, in the presence of THF, nickel stabilizes the primary products — carboxylates (ArCOOMgX) — in the form of their anion radicals. Ketyl radicals (Ar—CO$^{\dot{-}}$—R) are observable on adding HMPA to the reaction system, or on carrying out the reaction in the absence of THF. The specific formation of the anion radicals of the carboxylates on using THF, in contrast to many other investigated solvents, is not explicable at present. The g values of the anion radicals of the carboxylates are 2.004_0. Replacing nickel, with a nuclear spin of zero, by cobalt with $I = 7/2$ shows no evidence from the e.s.r. spectrum for the transfer of unpaired spin density to the cobalt nucleus. If the stabilization of radicals on the transition metal is considered, the absence of the interaction with the cobalt nucleus in the e.s.r. spectrum implies the π form of the radicals.

5. Anion radicals of β diketonates

In the reactions of nickel(II) chelates (acetylacetonate, benzoylacetonate, dipyvaloylmetanate, and 2,6-dimethyl-3,5-heptadionate) with Grignard reagents the formation of stable anion radicals of the corresponding chelate ligands was observed [6, 24, 25]. The splitting constants obtained by the simulation of experimental spectra are given in Table 9. Their assignment resulted from the variously substituted structures *XLII—XLV* [24]. Remarkable feature of the spectrum *XLIV* is C-13 satellites of methyl groups with $a_{\mathrm{C\text{-}13}} = 0.63$ mT.

Table 9

Structures and assignment of splitting constants of anion radicals from β diketonates

	Structures	Splitting constants, mT		
		a^1_{H}	a^2_{H}	$a_{\mathrm{H,C\text{-}13}}$
XLII		0.26	1.25	—
XLIII		0.275	0.075	—
XLIV		0.277	0.013	$a^3_{\mathrm{C\text{-}13}}$ 0.63
XLV		0.245	0.77	a_{H} *o* 0.335 *o'* 0.315 *m* 0.11 *p* 0.4

The stability as well as the spin distribution of unpaired electron of the investigated radicals depends considerably on the employed solvents as stated in Part 7. The Grignard reagents do not participate here in the formation of radical structure as the hyperfine splittings of e.s.r. spectra are independent of the employed reagents, *e.g.* (Me—, Et—, n-Pr—, and Ph—)MgBr or n-PrMg(—Cl, —Br, —I), this in contrast to the ketyl radicals described in Part 3. The Grignard reagents and the transition metal present in the system enable the transfer of electron to the chelate ligand and stabilize the so formed radicals.

In order to elucidate the role of the transition metal in the stabilization of β diketonates anion radicals, nickel with zero nuclear spin was replaced by cobalt having $I = 7/2$. But no splittings indicating the interactions of cobalt nucleus with the radicals were found in e.s.r. spectra. Further, we considered the unpaired spin density distribution of the anion radical *XLII* and its stabilization with counter ions Li^+ and MgX^+ by INDO calculations. The best agreement between calculated and experimental splitting constants was obtained for free anion radical [6]. These calculations have been expanded taking into account also Ni(II) and are summarized below and described in more detail in [24].

6. Anion radicals of sulfones

In the reaction of diphenylsulfone with n-BuLi the anion radical of diphenylsulfone *XLVI* is formed which undergoes the cross-coupling under the formation of dibenzothiophenesulfone anion radical *XLVII* [26]. These investigations were then expanded to the 4,4′-dimethyl-, 4,4′-diethyl-, 4,4′-di-t-butyl-, and 4,4′-di-i-propyl-dibenzothiophenesulfone and anion radicals of alkyl-substituted dibenzothiophenesulfones *XLVIII—LI* were obtained [27]. The splitting constants obtained by the simulation of experimental e.s.r. spectra of *XLVI* were: $2 \times a_4 = 0.479$ mT, $4 \times a_2 = 0.217$ mT, and $4 \times a_3 = 0.057$ mT, and those of structures *XLVII—LI* are summarized in Table 10. Additionally, spectrum of *LI* shows C-13 satellites assigned to the carbon nuclei of methyl groups with splitting constant $a_{C\text{-}13} = 0.38$ mT.

An open question in these reactions remains the mechanism of the cross-coupling. When the reaction proceeds in polar solvents like HMPA, the cross-coupled product *XLVII* with a yield up to 50 % was obtained. On the addition of nonpolar solvents like benzene or hexane to such systems, prior to the cross-coupled product *XLVII*, the anion radical of the original diphenylsulfone *XLVI* was observed. The conversion of *XLVI* to *XLVII* proceeds immediately on the addition of HMPA. We assume that in the first reaction step the anion radical $Ph_2SO_2^{\dot{-}}$ is formed according to the reaction scheme

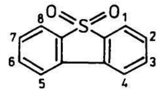
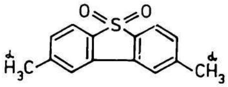
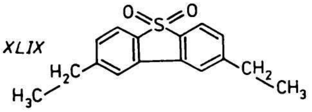
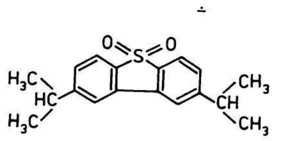
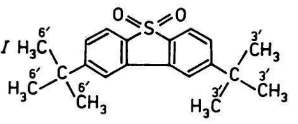
$$Ph_2SO_2 + \text{n-BuLi} \rightarrow Ph_2SO_2^{\dot{-}} + Li^+ + Bu^{\cdot}$$

In the next step the reactive butyl radical $Bu^{\cdot}$ abstracts hydrogen from the phenyl group and so initiates the cross-coupling. The analysis of the reaction mixture confirms the formation of butane.

The assignment of the splitting constants as given in Table 10 resulted from the analysis of the splittings in e.s.r. spectra of *XLVII* and its alkyl-substituted derivatives *L* and *LI*. By radical *LI*, substituted with t-butyl group in position 3,6, the splitting attributed to $a_{3,6}$ is absent in the spectrum and by *L*, similarly substituted with isopropyl group, $a_{3,6}$ decreases to 0.065 mT as expected for

Table 10

Assignment of the by experiment (and INDO calculations)*
obtained splitting constants

Anion radical		Splitting constants, mT				
		$a_{H}^{1,8}$	$a_{H}^{2,7}$	$a_{H}^{3,6}$	$a_{H}^{4,5a}$	$a_{C-13}^{3',6'}$
XLVII		0.020 (0.071)*	0.283 (0.261)*	0.206 (0.185)*	0.026 (0.095)*	— —
XLVIII		>0.033	~0.3	~0.2	>0.033	—
XLIX		>0.027	~0.3	~0.17	>0.027	—
L		0.045	0.3	0.065	0.045	
LI		0.036	0.289	—	0.036	0.38

methine proton in isopropyl group. Herewith, the splitting constants with the highest values can be assigned to the protons in position 2,7.

Considering the papers [28, 29] we re-analyzed the investigated sulfone anion radicals by INDO calculations [27] and obtained the splitting constants for *XLVII* as given in Table 10, which are in a relatively good agreement with experiment. By the INDO method [30] here calculated Wiberg's indexes point to the aromatic character of benzene rings, whereas the C—S, S—O, and C—C bonds on the cross-linked positions correspond, approximately, to a single bond. The charge is mostly (50 %) localized on the SO_2 group under a strong $\overset{\delta+}{S}$—$\overset{\delta-}{O}$ polarization. In contrast to that the unpaired spin density is mainly localized on the benzene rings and its smaller part (25 %) on the SO_2 group.

7. Solvent effect on the formation and stability of investigated radicals

The systematic studies of solvent effects in the above-described systems are limited by different stability of radicals in various solvents. Frequently, similar radicals are unstable in the same solvent and so for individual radicals another solvent has to be used. Therefore, the exact evaluation and comparison of solvent effects on the stability and distribution of unpaired spin density was possible only for some groups of radicals.

The attempts to generate the anion radicals of acetylacetonate (structure *XLII*; Table 9) in benzene, toluene or similar solvents were not successful because of its instability. In contrast to that, in etheric solvents, high radical concentrations and well resolved e.s.r. spectra were observable for longer time (in tetrahydrofuran solutions up to 10^{-3} mol dm^{-3} for some days) [6]. The splitting constant a_1 of methine proton shows an expressive solvent dependence in contrast to a_2 of methyl protons, which is practically independent of the employed solvents (Table 11). This suggests a strong interaction of solvent dipoles with the π system of anion radical.

Table 11

Splitting constants and g values of the acetylacetonate anion radical in different solvents

The reaction mixture consisted of 25 volume % of diethyl ether, 25 volume % of toluene, and 50 volume % of the solvent in question

Solvent	Splitting constants, mT		
	a_1	a_2	g value
a Diethyl ether	0.425	1.305	2.004_2
b Diisopropyl ether	0.35	1.30	2.004_1
c Tetrahydrofuran	0.26	1.25	2.004_1

Further systematic studies on solvent effects were carried out in the reactions of benzenecarboxylic acids (ArCOOH) with phenylmagnesium bromide (PhMgX) [31], where the formation of aryl aryl ketyl radicals (Ar—$CO^{\dot{-}}$—Ph) was observed. The investigated solvents, according to their influence on the radical formation and on the distribution of unpaired electron, can be divided into two groups. To the first group belong such solvents as Et_2O, i-Pr_2O, n-Bu_2O, t-BuOMe, hexane, cyclohexane, benzene, toluene, and triethylamine and to the second one dimethoxyethane (DME), dioxan, and hexamethylphosphortriamide (HMPA). The volume ratio of the investigated solvent was varied from 10 to 80% relative to Et_2O — always present in the system. E.s.r. spectra suitable for evaluation were observed only for the structures *LII* and *LIII* with a limited number of solvents; their splitting constants of protons are given in Table 12.

In the first group of solvents the radicals are formed at the ratio ArCOOH : PhMgX = 1 : 4 and in the second group this has to be increased to 1 : 8. The radicals in the first group are characterized by splitting constants given in Table 12 for Et_2O and toluene and are practically independent of the employed solvent. In contrast to that, the solvents of the second group influence the distribution of unpaired spin density and increase the splitting constants in *ortho* and *para* position and decrease them in *meta* position. The radical concentration up to 10^{-4} mol dm^{-3} in the first group remains at the laboratory temperature unchanged for 1—2 days. In the second group radicals are stable for more days but their formation is observed only if the ratio of the investigated solvent is lower than 60 % in the system.

The influence of solvents on the stability and the distribution of unpaired density of radicals is a very complex problem reflecting various properties of solvents as well as radicals, *e.g.* their acid-base and steric properties, coordination ability, and other similar ones. These properties frequently exhibit opposite effects, therefore it is generally difficult to find a straight correlation between the changing values of splitting constants or stability of radicals and some properties of the investigated solvents.

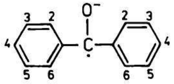
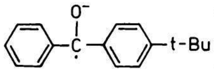
Further problems involving solvent effects are described in other parts of this contribution and cited references, *e.g.* by the formation of various nickel valence states (Part 1, Ref. [5, 7—10]), formation of the carboxylate anion radicals (Part 4, Ref. [23]), sulfone anion radicals (Part 6; Ref. [26, 27]), by the modification of reduction power of organometallic compounds (Part 8; Ref. [32]).

8. New possibilities in the generation of anion radicals

The generation of anion radicals by means of organometallic compounds and transition metals according to the procedure described in [32], based on the mixing of the substrate solution with the solution of organometallic compound, was carried out successfully with many different substances. This is illustrated in Fig. 2 and Table 13 with aldehyde (*LIV*), ketones (*LV*, *LVI*, *LX*), enolates of β-diketones (*LVII*, *LVIII*), quinone (*LXII*), α-diketone (*LXI*), sulfone (*LIX*), nitrobenzene (*LXIII*), cyano compounds (*LXIV*, *LXV*), aromatic hydrocarbons (*LXVI*—*LXVIII*), and heteroaromatics (*LXIX*—*LXXI*). The experimental and simulated e.s.r. spectra of the corresponding anion radicals are represented along with their splitting constants and peak-to-peak widths in Table 13, Fig. 2; Ref. [32, 33]. In a similar way anion radicals were generated from many other substances, such as

Table 12

Influence of solvents on the proton splitting constants of aryl aryl ketyl radicals

Structures		Solvent	Splitting constants, mT									
			a_2	a_3	a_4	a_5	a_6	a_2	a_3	a_4	a_5	a_6
LII		DME	0.318	0.117	0.359	0.117	0.305	0.318	0.117	0.359	0.117	0.305
		HMPA	0.290	0.102	0.358	0.102	0.290	0.290	0.102	0.358	0.102	0.290
LIII		Et$_2$O	0.255	0.125	0.282	0.125	0.255	0.228	0.125		0.125	0.228
		Toluene	0.253	0.130	0.285	0.130	0.253	0.235	0.130		0.130	0.235
		Dioxan	0.327	0.117	0.367	0.117	0.327	0.305	0.117		0.117	0.305
		DME	0.325	0.118	0.375	0.118	0.325	0.300	0.118		0.118	0.300
		HMPA	0.306	0.103	0.383	0.103	0.306	0.271	0.103		0.103	0.271

nitrobenzene, diazobenzene, sulfoxides, phosphines, *etc.* To simplify the identification of the radicals chosen for illustration in Fig. 2 and Table 13, the generation of

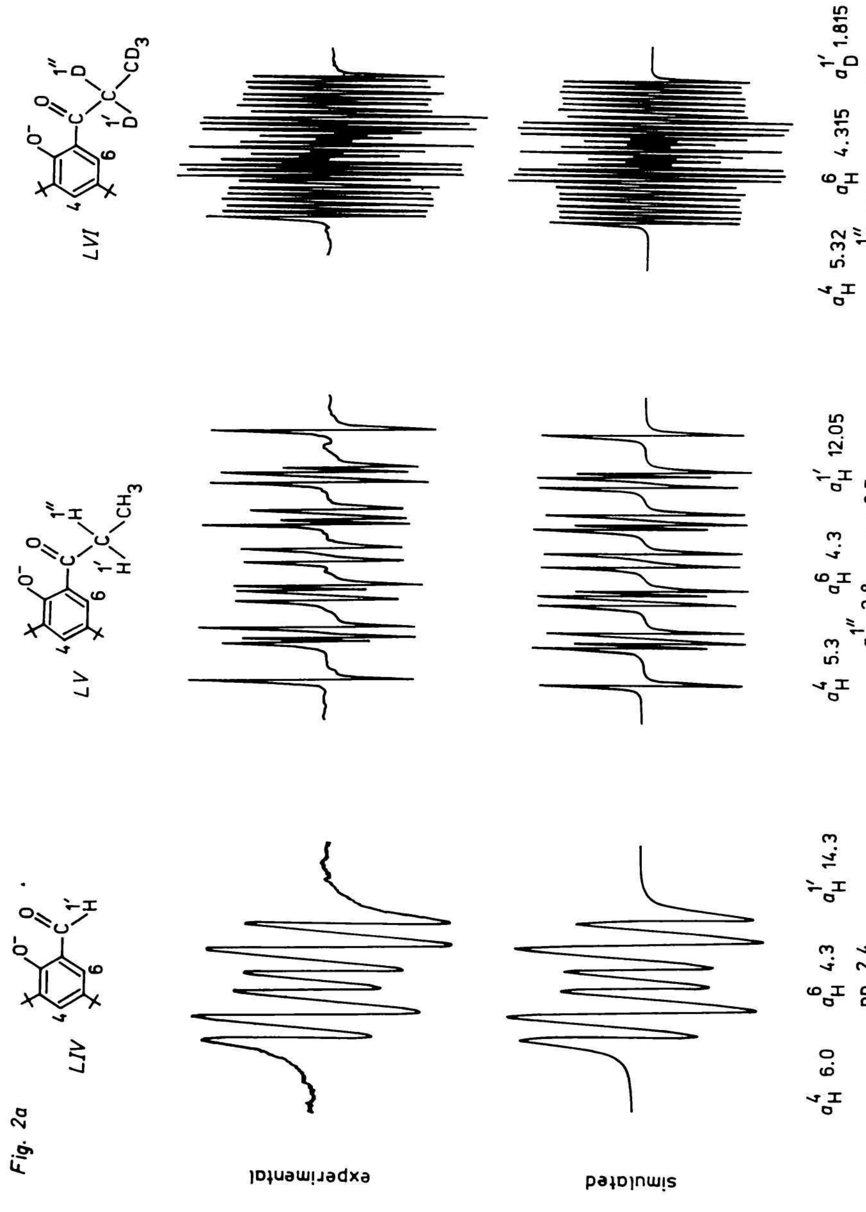
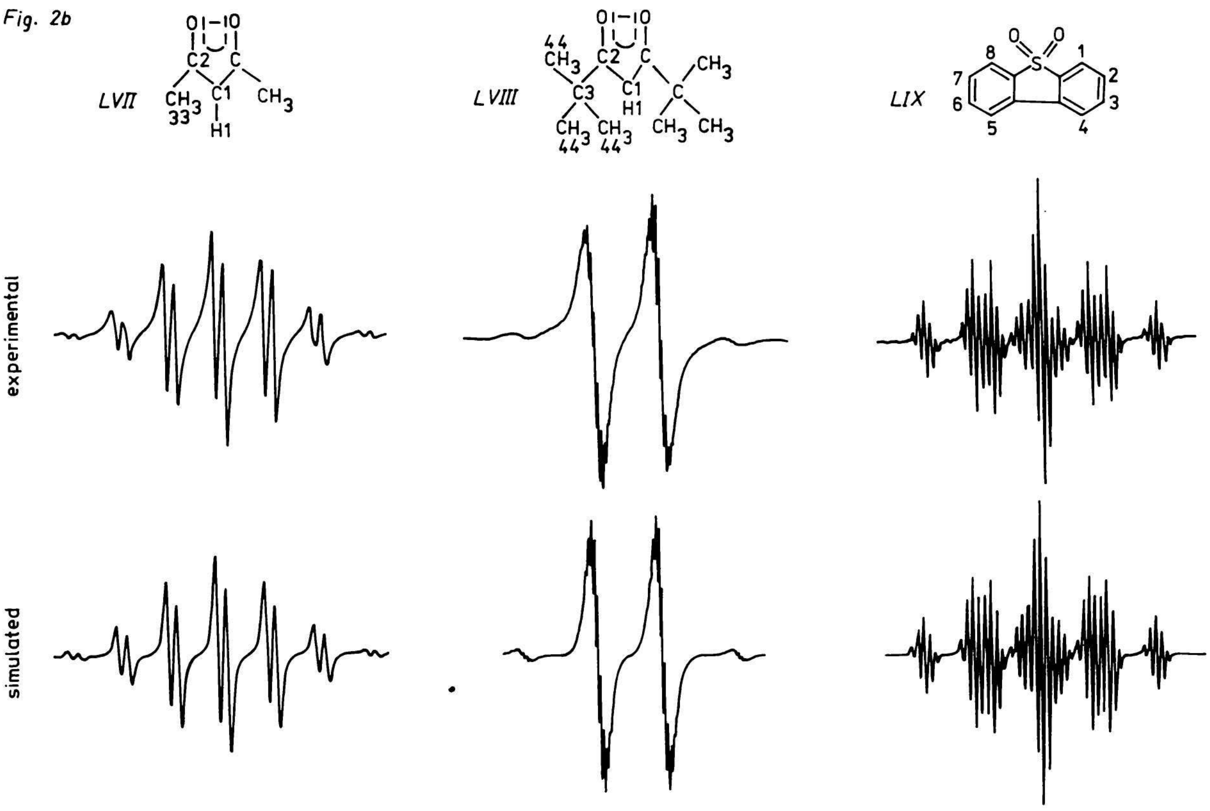


Fig. 2a



a_H^1 2.6 $6 \times a_H^3$ 12.3 pp 1.45

93.4%: a_H^1 2.77 $18 \times a_H^4$ 0.13 pp 0.125
6.6%: a_H^1 2.77 $18 \times a_H^4$ 0.13 $a_{^{13}C}^4$ 6.3

$a_H^{2,7}$ 2.8 $a_H^{3,6}$ 2.05 $a_H^{1,4,5,8}$ 0.24
pp 0.1

Fig. 2. Splitting constants a_H and a_N and peak-to-peak widths obtained by the simulation of the spectra of anion radicals generated by means of organometallic compounds (a_H, a_N, and pp expressed in 0.1 mT)

Table 13

Splitting constants a_H and a_N and peak-to-peak widths obtained by the simulation of the spectra of anion radicals generated by means of organometallic compounds

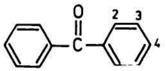
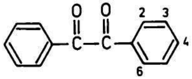
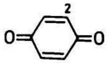
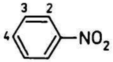
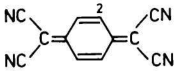
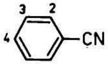
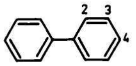
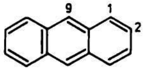
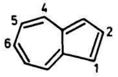
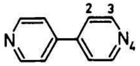
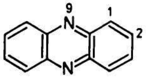
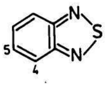
Anion radical		Splitting constants, mT								
		a_N	a_H^1	a_H^2	a_H^3	a_H^4	a_H^5	a_H^6	a_H^9	pp
LX		—	—	0.284	0.104	0.343	—	—	—	0.018
LXI		—	—	0.096	0.035	0.112	—	0.104	—	0.019
LXII		—	—	0.235	—	—	—	—	—	0.02
LXIII		1.095	—	0.340	0.110	0.390	—	—	—	0.04
LXIV		0.0995	—	0.140	—	—	—	—	—	0.018
LXV		0.207	—	0.342	0.02	0.819	—	—	—	0.01

Table 13 (Continued)

Anion radical	Splitting constants, mT								
	a_N	a_H^1	a_H^2	a_H^3	a_H^4	a_H^5	a_H^6	a_H^9	pp
LXVI 	—	—	0.262	0.0415	0.525	—	—	—	0.013
LXVII 	—	0.271	0.15	—	—	—	—	0.52	0.013
LXVIII 	—	0.029	0.394	—	0.602	0.1255	0.861	—	0.012
LXIX 	0.3595	—	0.242	0.0385	—	—	—	—	0.013
LXX 	0.506	0.193	0.152	—	—	—	—	—	0.018
LXXI 	0.511	—	—	—	0.283	0.157	—	—	0.02

the anion radicals was mainly carried out on some basic, well known structures. The splitting constants of the investigated radicals obtained here are identical or close to those cited in papers [32, 33] and justify the identification of the radicals.

Before discussing the generation of the anion radicals, it should be noted that the influence of the solvents, the organometallic compounds, and the transition metals on the yield and type of radicals generated is a very complex problem. In order to discuss it the investigated radicals have been divided into three groups, although there are no sharply defined differences between them.

Aromatic hydrocarbons and heteroaromatics (*LXVI—LXXI*)

A suitable solvent for this group is HMPA with n-BuLi as the organometallic compound. In many cases the transition metals influence the radical generation only to a negligible extent.

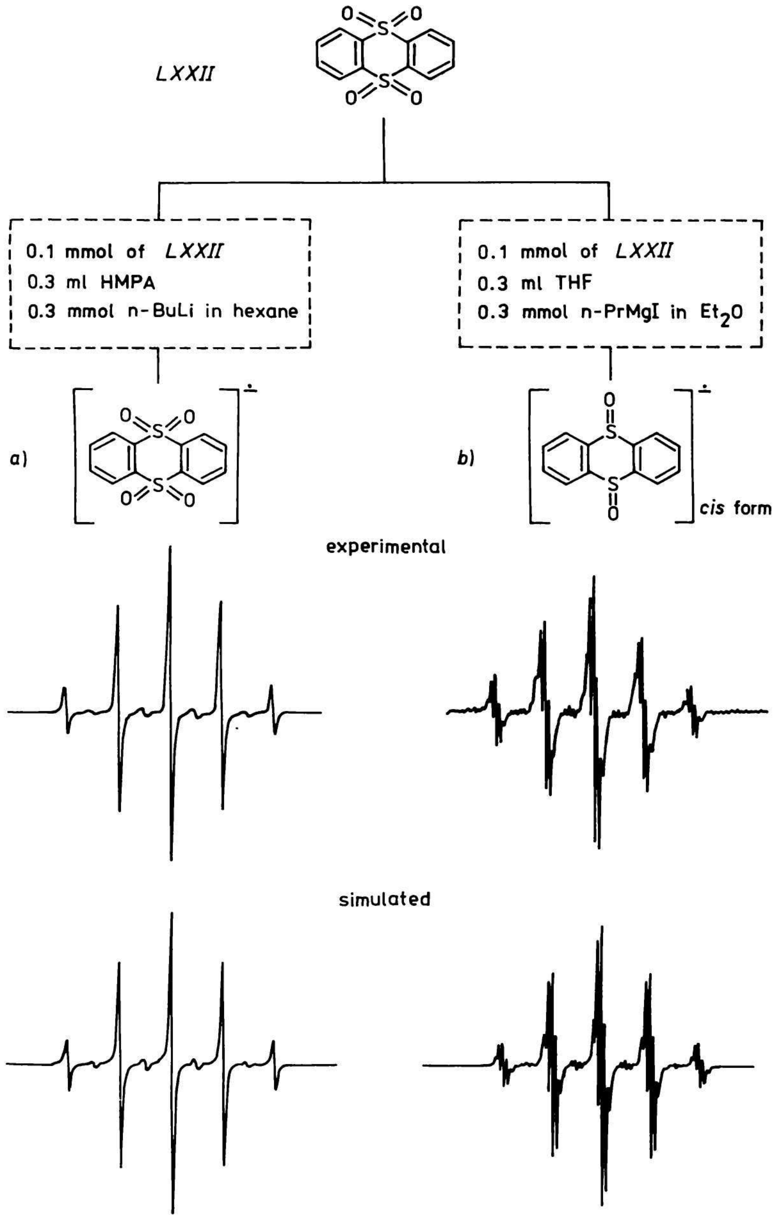
Compounds with different functional groups (*LIX—LXV*)

This group includes quinones, ketones, α-diketones, sulfones, nitro and cyano compounds. For these compounds different solvents and organometallic compounds may be used, but they, together with the transition metals, considerably modify the yield and the type of generated radicals.

The influence of the solvents (HMPA or THF) and the organometallic compounds (n-BuLi or n-PrMgI) on the type of anion radicals generated from thianthrene-5,10-tetroxide (*LXXII*) is shown in Fig. 3. Employing HMPA and n-BuLi, anion radical *LXXIIa* was generated and identified as the anion radical of thianthrene-5,10-tetroxide. Using THF and n-PrMgI, however, anion radical *LXXIIb* was observed, identified as the anion radical of thianthrene-5,10-dioxide. This was verified in another experiment employing thianthrene-5,10-dioxide, THF, and n-PrMgI, where also the spectrum *LXXIIb* was obtained.

According to our experience, the system HMPA—BuLi possesses very moderate reduction power, and usually transfers only one electron to the substrate added to it, without a further consequent reaction. Therefore, in such system it is possible to generate the anion radicals for substances with the functional groups in a high oxidation state such as nitrates, sulfones, and quinones. On the other hand, systems such as ethers—RMgX are more reactive and frequently lead to a consequent reduction of the substrate which is observable from the anion radicals of the reduction products.

The influence of transition metals on the concentration and the type of radicals generated is very complex and it depends on the type of substrate, the solvents, the



95.6 %: $4 \times a_{\mathrm{H}}$ 2.15 pp 0.14

4.4 %: $4 \times a_{\mathrm{H}}$ 2.15 $a_{^{13}\mathrm{C}}$ 2.05

95.6 %: $4 \times a_{\mathrm{H}}$ 2.04 $4 \times a_{\mathrm{H}}$ 0.155 pp 0.1

4.4 %: $4 \times a_{\mathrm{H}}$ 2.04 $4 \times a_{\mathrm{H}}$ 0.155 $a_{^{13}\mathrm{C}}$ 2.04

Fig. 3. Experimental and simulated e.s.r. spectra of anion radicals generated from thianthrene-5,10-tetroxide by means of n-BuLi in HMPA (*LXXIIa*) and n-PrMgI in THF (*LXXIIb*) along with splitting constants (a_{H}, a_{C}) and peak-to-peak widths (pp) of simulated spectra, expressed in 0.1 mT.

organometallic compounds, and on the type and concentration of the transition metal. The following metals Mn, Fe, Co, Ni, and Cu were investigated, employing their halogen compounds or chelates, as described in [32, 33]. The ratio between the substrate and transition metal was usually 10:1. In most cases, *e.g.* with substrates *LIX—LXV*, a 5—50-fold increase of radical concentration was obtained if transition metals were employed. In some cases, as illustrated below on substrate *LXXIII*, the presence of a transition metal modified the radical products.

Fig. 4 illustrates the influence of nickel on the type of anion radical generated from tetracyanoethylene (*LXXIII*) with n-PrMgI. In the presence of $NiBr_2$ or $CoBr_2$, spectrum *LXXIIIa* was obtained. It was simulated, assuming the interaction of four equivalent nitrogen atoms with the unpaired electron having a splitting constant $a_N = 0.1575$ mT. In accord with the literature [34] spectrum *LXXIIIa* was assigned to the anion radical of *LXXIII*, but, in the absence of transition metal spectrum *LXXIIIb* was obtained. This was simulated by means of one splitting constant of one nitrogen atom $a_N = 0.1245$ mT and by one splitting constant of three equivalent atoms $a_N = 0.1695$ mT. To investigate the participation of organometallic compounds in the formation of radical structure *LXXIIIb*, the generation was undertaken employing (CH_3—, C_2H_5—, C_2D_5—, and n-C_3H_5)MgBr. For all Grignard reagents employed, a spectrum similar to *LXXIIIb* was obtained. Since the atoms of the Grignard reagents do not contribute to the spectral structure *LXXIIIb*, its origin has to be in the tetracyanoethylene molecule having, under given conditions, nonequivalent nitrogen atoms. Such type of anion radicals generated from tetracyanoethylene has not been described so far, and the nonequivalence of the nitrogen atoms of this symmetrical molecule deserves attention. A possible explanation for this can be a relatively strong coordination of one cyano group of the tetracyanoethylene anion on the magnesium cation. Consequently, the unpaired spin density of this group and the splitting constant ($a_N = 0.1245$ mT) of its nitrogen atom decreases. The three remaining cyano groups possess higher spin density than the group mentioned, with approximately equal splitting constants for their nitrogen atoms ($a_N = 0.1695$ mT).

The role of transition metal in such system is discussed in Part 9. Finally, it might be added, that in a relatively simple procedure, employing organometallic compounds and transition metals, the generation of anion radicals for various structural types was possible. This method of radical generation can be useful in many applications and further systematic studies of such systems may widen the scope of this phenomenon to many other fields.

9. The role of transition metal in the formation and stabilization of the investigated radicals

In the most above-described systems the presence of transition metal was required to observe the formation of anion radicals. The role of nickel is obvious

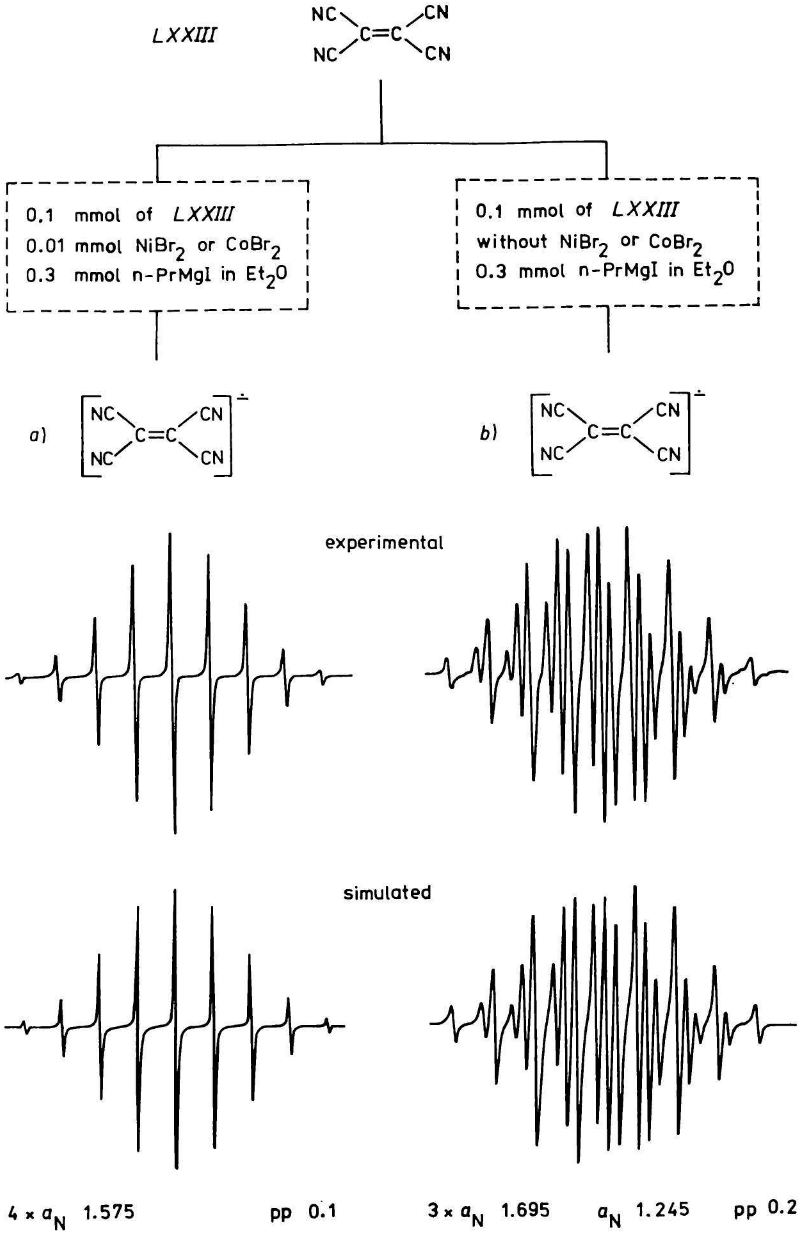


Fig. 4. Experimental and simulated e.s.r. spectra of anion radicals generated from tetracyanoethylene in the presence of $NiBr_2$ or $CoBr_2$ (*LXXIIIa*) and without transition metals (*LXXIIIb*) along with splitting constants (a_N) and peak-to-peak widths (pp) of simulated spectra, expressed in 0.1 mT.

when the following three experiments of nickel(II) 3,5-diisopropylsalicylate ($NiDIPS_2$) resp. 3,5-diisopropylsalicylic acid (HDIPS) in the reaction with n-BuMgBr are compared

a) HDIPS + n-BuMgBr

b) HDIPS + $NiCl_2$ + n-BuMgBr (HDIPS : Ni = 10 : 1)

c) $NiDIPS_2$ + n-BuMgBr

In experiment *a*) *i.e.* without transition metal, no radical formation was observed. In *b*), on the addition of definite amount of $NiCl_2$ to the system, the radical concentration increased up to 10^{-3} mol dm^{-3} and then remained constant on the further addition of nickel. In experiment *c*) *i.e.* in the presence of nickel, the formation of radicals in high concentrations was observed immediately after mixing the reactants. Similar behaviour was observed employing another chelated compounds and transition metals (Fe, Co). From these experiments it is evident that the presence of transition metals facilitates the radical formation. In the case of nickel, this radical formation was also facilitated when Ni(II), before its addition to the reaction mixture, was reduced by organometallic compounds to Ni(0). Therefore, it is probable that nickel in its zero valence state mediates the transfer of one electron to the substrate S according to the reaction scheme

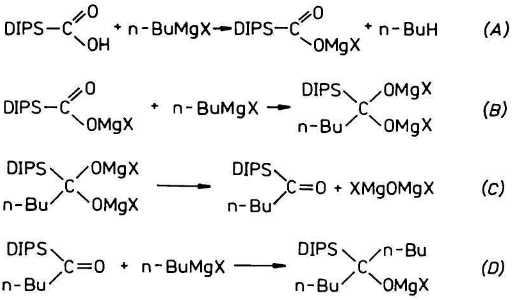
$$\mathrm{Ni(0)} + \mathrm{S} \rightarrow \mathrm{Ni(I)} + \mathrm{S}^{\dot{-}}$$

$$\mathrm{Ni(I)} + \mathrm{R}^{-} \rightarrow \mathrm{Ni(0)} + \mathrm{R}\cdot$$

It cannot be excluded that nickel, also in its higher valence states, mediates the transfer of electron to the substrates S. The proportionality of the anion radical concentration to the concentration of nickel implies the possibility of complex formation between the radical and transition metal. However, employing cobalt as the transition metal here and also by anion radicals described in Parts 3—5, brought no evidence for an interaction between the unpaired electron and the cobalt nucleus in the e.s.r. spectra.

In order to elucidate more complexly the role of nickel in such systems, the analysis of the products in the reaction of HDIPS with n-BuMgBr in the presence of nickel salts was carried out [35]. According to the liquid chromatographic analysis the hydrolyzed reaction mixture contains eight compounds. In their separation by means of column chromatography, besides HDIPS, following major products were isolated and identified by ^{1}H-n.m.r. spectroscopy: 2-hydroxy-3,5-diisopropylphenyl n-butyl ketone and 2-hydroxy-3,5-diisopropylphenyl di-n-butyl carbinol. The products of pinacol type are expected in such reactions but were not found in the reaction mixture. The obtained results confirm the formation of keto products in the presence of nickel.

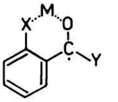
Generally, Grignard reagents in their reactions are added to ketones under the formation of the corresponding tertiary alcohols [36]. In accord with this generalization, in experiment *a*) *i.e.* in the absence of nickel, keto products were not found and the following scheme should be expected in the reaction of HDIPS (in the scheme it is reformulated as DIPSCOOH) with n-BuMgX



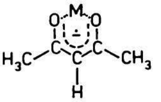
Reaction *D* proceeds probably much quicker than the previous reaction steps, therefore, the commonly obtained products are the corresponding tertiary alcohols also at the low ratios of Grignard reagents to acids. To prepare ketones in this way successfully, it is necessary to eliminate reaction *D* or to lower its reaction rate.

For the role of nickel in such reactions two explanations may be taken into account. The first one would propose the acid properties of nickel and consequently a rapid acceleration of reaction *A* compared to the rate of reaction *D*. So it came to the accumulation of the keto products in the reaction mixture. In the second explanation the stabilization of the obtained keto products in the form of their ketyl radicals is assumed. Now, it is known that the acid properties of nickel are very weak. But also salts with stronger acid properties than nickel, as *e.g.* $FeCl_3$, were employed and showed to be less effective than nickel. Therefore, the explanation proposing the acid catalysis of transition metals in the reaction is not probable. Our experimental data are very well compatible with the assumption that nickel stabilized the keto products in the form of their ketyl radicals, herewith, it eliminates a further addition of Grignard reagents and the formation of tertiary alcohols.

The possible ways in the stabilization of the investigated anion radicals by various counter ions M (H^+, Li^+, $MgCl^+$, Ni(0), $NiCl_2$ resp. $NiCl_3^-$) were investigated by INDO calculations for the common structures *LXXIV* [21] and *LXXV* [6, 24]



LXXIV



LXXV

where Y was alkyl or aryl group and X was —H or $—O^-$. The best agreement between the experimental and calculated splitting constants was obtained for Ni(II) compounds.

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