

**Paramagnetic species in the reactions
of organometallic reagents. VI.*
High-resolved e.s.r. spectra of anion radicals**

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High-resolved electron spin resonance spectra of anion radicals of substrates as ketones, enolates of β -diketones, quinones, sulfones, sulfoxides, nitro and cyano compounds, aromates and heteroaromates were obtained in a relatively simple procedure employing organometallic compounds as reduction agents. Experimental and simulated spectra are presented and some general aspects of this new method in the generation of anion radicals are discussed.

Получены спектры ЭПР высокого разрешения для анионных радикалов таких субстратов, как кетоны, энольные формы β -дикетонов, хинонов, сульфонов, сульфоксидов, нитро- и циано-соединений, ароматов и гетероароматов при помощи относительно простого метода, использующего в качестве восстановителя металлорганические соединения. Представлены экспериментальные и смоделированные спектры. В связи с указанным новым методом получения анион-радикалов обсуждаются некоторые вопросы общего порядка.

Previously we reported that during the reduction of salicylic acids with Grignard reagents in the presence of transition metals the formation of ketyl radicals was observed [1—4]. Analogously, in the reactions of transition metal chelates with organometallic compounds the anion radicals of chelate ligands were obtained [5]. Then, a further extension of this technique enabled us to generate the anion radicals on various structures [1]. In this paper high-resolved experimental and simulated e.s.r. spectra obtained by this new method are presented and some general aspects of its application in the generation of anion radicals are discussed.

* For Part V see Ref. [1].

Experimental

Chemicals

The origin of solvents, their handling and purification as well as the origin of substances VI—XVIII (Fig. 1) and organometallic compounds were described previously [1]. Other substances were prepared according to the following references: 5-mono-*tert*-butyl-salicylic acid (HMTBS) [6], nickel(II) benzoylacetone [Ni(Bzac)₂] [7], dibenzothiophene sulfone [8], thianthrene-5,10-disulfoxide [9], and nickel(II) acetylacetonate [Ni(acac)₂] [10].

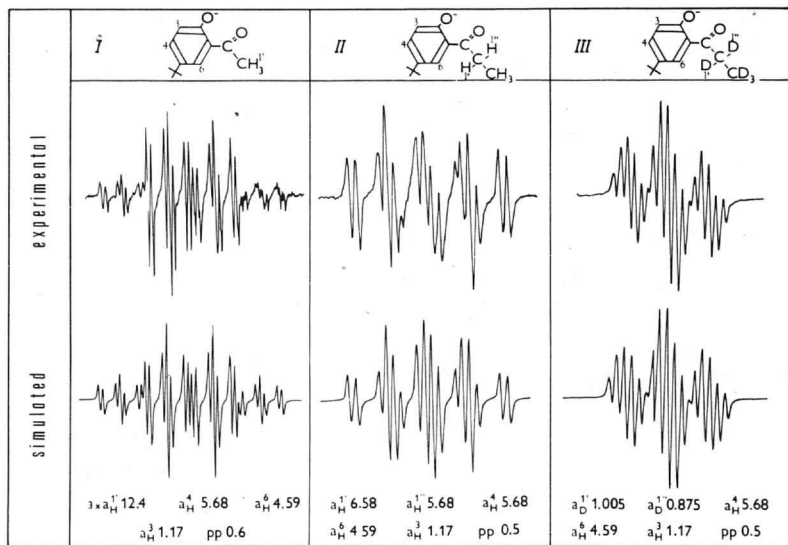


Fig. 1. Experimental and simulated spectra of anion radicals generated by means of organometallic compounds. (Fig. 1 continued, see pp. 296—298.)

a_H , a_D , a_N are splitting constants and pp peak-to-peak widths of simulated spectra expressed in 0.1 mT.

Procedure

The e.s.r. tubes and all reservoirs for the solvents and solutions were equipped with three-way-cocks and kept under argon atmosphere. The transfer of reactants from reservoirs into e.s.r. tubes was carried out by syringe under a strong argon stream blown through the three-way-cocks. The spectra of compounds I—XVIII (Fig. 1) were obtained when mixing the following reactants in the e.s.r. tube: structures I—III 0.2 ml of 0.5 M-HMTBS in Et₂O, 0.1 ml of 0.1 M-Ni(acac)₂ in benzene and then 0.2 ml of 2 M-RMgX in Et₂O were added (CH₃MgBr to I, C₂H₅MgBr to II, and C₂D₅MgBr to III); structure IV 0.2 ml of 0.1 M-Ni(Bzac)₂ in benzene and 0.2 ml of 2 M-*n*-PrMgI in Et₂O; structure V 10⁻⁴ mole of

dibenzothiophene sulfone, 0.2 ml hexamethylphosphortriamide (HMPA), 0.2 ml of 1 M-*n*-BuLi; structure VI 10^{-4} mole thianthrene-5,10-disulfoxide, 0.2 ml tetrahydrofuran (THF), 0.2 ml of 2 M-*n*-PrMgI in Et₂O. The generation of the anion radicals of the remaining structures VII—XVIII was described in [1] and the assignment of splitting constants was undertaken in accord with the following references: VII [11], VIII [12], IX [13], X [14], XI [15], XII [16], XIII [17], XIV [18], XV [19], XVI [20], XVII [21], XVIII [22].

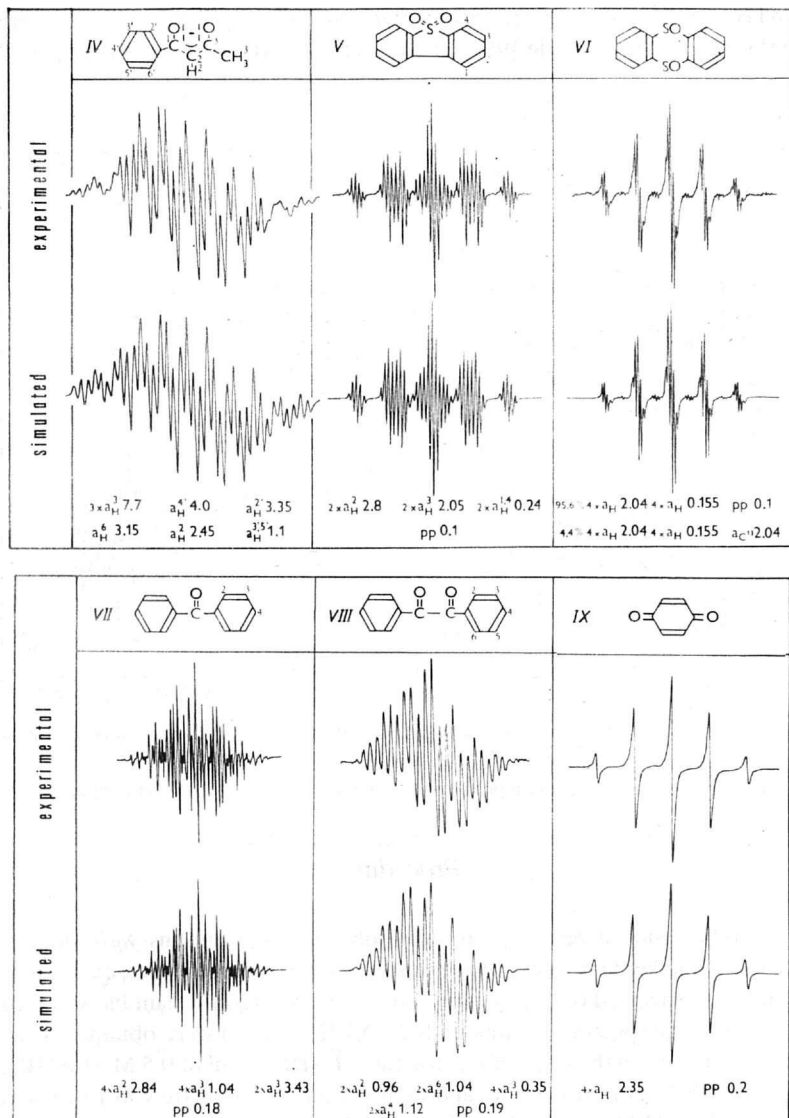


Fig. 1 (Continued)

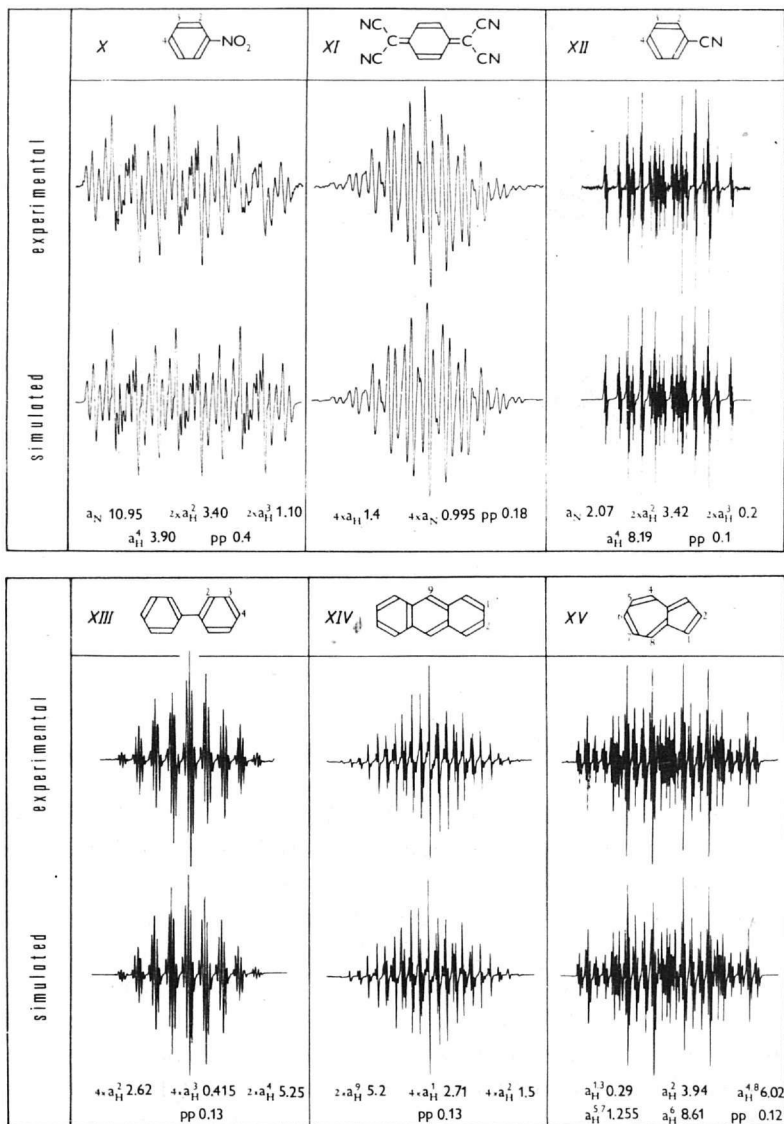


Fig. 1 (Continued)

Measurements

The experiments were carried out at 20°C and the e.s.r. spectra measured and simulated on a Varian E-3 Spectrometer equipped with a Computer Varian Spectra System SS 100.

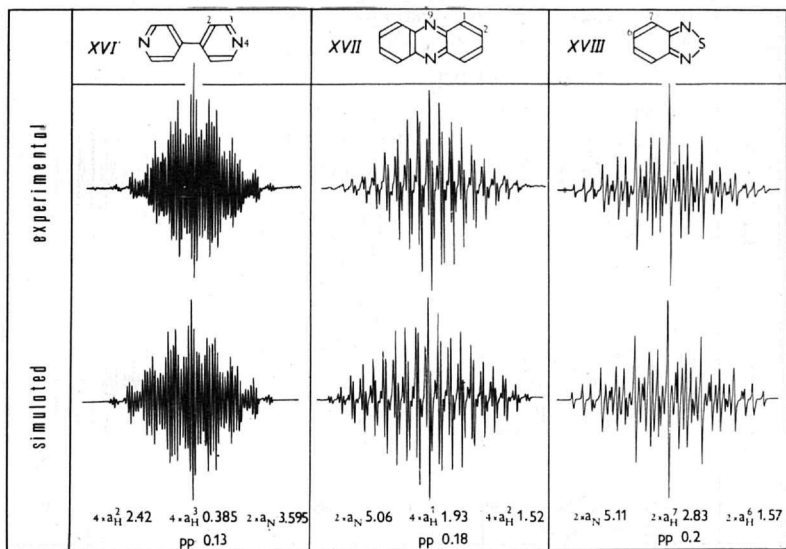


Fig. 1 (Continued)

Results and discussion

Identification of radical structures and assignment of their splitting constants

By the reactions of 5-mono-*tert*-butyl-salicylic acid with Alkyl-Grignard reagents in the presence of transition metal products *I*, *II*, and *III*, with their e.s.r. spectra as given in Fig. 1, were obtained. The observed radical formation can be explained analogously as it was in more details described in our previous studies [2, 3]. In accord with those studies we assume that in the reactions of 5-mono-*tert*-butyl-salicylic acid with Alkyl-Grignard reagents the carboxyl group is reduced and the corresponding aryl alkyl ketone is formed. The transition metal present in the system mediates the transfer of one electron from the Grignard reagents to the so produced aryl alkyl ketone under the formation of its ketyl radical.

The formation of such ketyl radicals is confirmed by the analysis of the e.s.r. spectra in Fig. 1. In the case of structure *I* an interaction of three equivalent methyl protons originating from CH_3MgBr with the unpaired electron should be observed. Therefore, we assigned the splitting constant $3 \times a_{\text{H}}^1 = 1.24$ mT to the methyl protons. Then, the remaining splitting constants had to be assigned to the protons originating from salicylate as follows: the highest splitting constant ($a_{\text{H}}^4 = 0.568$ mT) to the *para*, then the lower ($a_{\text{H}}^5 = 0.459$ mT) to the *ortho*, and the lowest one ($a_{\text{H}}^3 = 0.117$ mT) to the *meta* proton. Such an assignment is also confirmed by structures *II* and *III*. We found there again the same values for

splitting constants a_{H}^3 , a_{H}^4 , and a_{H}^6 as they were given above and therefore assigned them to the protons of salicylate ring. Subsequently, the remaining splitting constants $a_{\text{H}}^{1'} = 0.658$ mT and $a_{\text{H}}^{1''} = 0.568$ mT found with the structure *II* can originate only from the methylene protons of the ethyl group. This is also in a very good agreement with structure *III*, where the ethyl group was replaced by its deuterated analogues and the expected changes of splitting constants were obtained ($a_{\text{H}}^{1'} = 0.658$ mT \rightarrow $a_{\text{D}}^{1'} = 0.1005$ mT and $a_{\text{H}}^{1''} = 0.568$ mT \rightarrow $a_{\text{D}}^{1''} = 0.0875$ mT). Remarkable here is the observed inequivalence of the methylene protons, which was also found and discussed with similar structures previously [3, 4].

The assignment of the splitting constants found with the anion radical of benzoylacetate (structure *IV*) is based on the results we obtained for acetylacetate [5]. The difference between these two structures is in one methyl group which is in the case of benzoylacetate replaced by phenyl group. Therefore, it can be assumed that a considerable part of unpaired spin will be transferred from the chelate ring to the phenyl group. In accord with this assumption we observed a considerable decrease of the splitting constant belonging to methyl protons of benzoylacetate ($3 \times a_{\text{H}}^3 = 0.77$ mT) comparing with that one of acetylacetate ($3 \times a_{\text{H}}^3 = 1.25$ mT). Based on this assumption too, the splitting constant $a_{\text{H}}^{2'} = 0.245$ mT was assigned to the methine proton of chelate ring of benzoylacetate, as with the acetylacetate this splitting constant was 0.26 mT, and in the simulated spectrum of structure *IV* there is no other alternative value (the other splitting constants are either too high or too low). Then still remain five splittings ($a_{\text{H}}^{4'} = 0.4$ mT, $a_{\text{H}}^{2''} = 0.335$ mT, $a_{\text{H}}^{6'} = 0.315$ mT, and $a_{\text{H}}^{3',5'} = 0.11$ mT) which belong to the protons of phenyl group. They were, in accord with the generally known redistribution of unpaired spin density on aromates, assigned as follows: the highest constant ($a_{\text{H}}^{4'}$) to the *para*, the next two highest ($a_{\text{H}}^{2''}$ and $a_{\text{H}}^{6'}$) to the *ortho*, and the lowest constant ($a_{\text{H}}^{3',5'}$) to the *meta* protons. The inequivalence of *ortho* protons suggests a hindered rotation of phenyl group and its approximative location in the plane of chelate ring. *Kwan* and *Kochi* [23] came also to a similar conclusion.

The anion radical of dibenzothiophene sulfone (structure *V*) was identified in accord with [24], where similar splitting constants as found in this work were obtained for a_{H}^2 ($a_{\text{H}}^2 = 0.261$ mT [24] and $a_{\text{H}}^2 = 0.28$ mT in this work) and a_{H}^3 ($a_{\text{H}}^3 = 0.215$ mT [24] and $a_{\text{H}}^3 = 0.205$ mT in this work). However, slightly different values were found in our experiments for the splitting constants a_{H}^1 and a_{H}^4 compared with [24] ($a_{\text{H}}^1 = 0.011$ mT, $a_{\text{H}}^4 = 0.024$ mT in [24] and $a_{\text{H}}^1 = a_{\text{H}}^4 = 0.024$ mT here). This deviation is probably due to the different method of the generation and the solvents employed (in [24] generation by means of potassium mirror in dimethoxyethane and in our experiments by means of *n*-BuLi in HMPA). Systematical investigations on differently substituted sulfones in various solvents are in progress and will be reported.

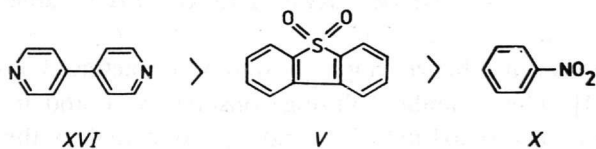
*Some general aspects of the generation of anion radicals
by means of organometallic compounds*

The question should be discussed how common the application of this new method in the generation of anion radicals is? As shown in Fig. 1, using this method it was possible to generate anion radicals of various basic structures with different functional groups. We also widen the application of this method to the more complex and variously substituted structures. Summarizing our experience it can be said that the concentration and the stability of anion radicals generated from the structures given in Fig. 1 increase with their analogues if they possess more extended π systems and a higher number of substituents. From this generalization are excepted the substituents with protolytic character like primary, secondary amino or phenoxy groups or strongly electronegative substituents like tertiary amino groups. The generation of stable anion radicals of some still simpler structures than those given in Fig. 1 like e.g. naphthalene, benzene or butadiene by this method appeared to be either impossible or very troublesome.

The technique described offers also a possibility to compare the relative stability of different anion radicals. This is obvious from a comparison of three experiments. In these experiments the anion radicals were generated by means of *n*-BuLi in HMPA as described in the general procedure, however, in the e.s.r. tube there were simultaneously more substances, namely,

- (i) XVI, V, X,
- (ii) V, X,
- (iii) X (numbers for the structures are taken from Fig. 1).

In each experiment we obtained e.s.r. spectrum of one compound, namely, in experiment (i) spectrum XVI, (ii) V, and (iii) X. From these results it can be concluded that under the given conditions the stability of anion radicals XVI, V, and X decreases as follows (Scheme 1)



Scheme 1

According to our experience a very important role of solvents in such systems should be stressed. A tight solvation of anion radicals rather more than the formation of contact ion pairs between anion radicals and their counter ions seems to be probable. It can be assumed that a fundamental requirement to obtain high-resolved e.s.r. spectra is a mutual isolation of the individual paramagnetic species in the solution by complexing agents. Such complex-forming properties can

be expected in the case of solvents possessing lone electron pairs e.g. like HMPA, ethers, etc. Some further aspects as the influence of solvents and the organometallic compounds on the generation of anion radicals as well as the problem of counter ions in such systems will be summarized later.

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