

ANION RADICALS OF BETA DIKETONATES*

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Formation of anion radicals $[\text{RCOCHCOR}']^{\dot{-}}$ with $\text{R} \equiv \text{R}' = \text{Me}$, *i*-Pr, *t*-Bu, and with $\text{R} = \text{Me}$, $\text{R}' = \text{Ph}$ has been observed in reactions of beta diketonates with Grignard reagents. The splitting constant of the methine proton is 0.26 mT, and that of the methyl protons is 1.2 mT if $\text{R} \equiv \text{R}' = \text{Me}$. According to INDO calculations the anion radical is stabilized with Ni^{+2} counterion in tetrahedral arrangement.

Within studies of catalytic systems of nickel chelates with organometallic compounds we described¹ the anion radical of 2,4-pentanedionate (acetylacetonate $\text{H} \text{acac}^{\dot{-}}$) formed in reaction of Niacac₂ with Grignard reagents. Similarly, formation of the anion radicals of beta diketonates was described in ref.² This communication extends the study to such ligands as 2,2,6,6-tetramethyl-3,5-heptanedionate (dipivaloyl methanate $\text{DPM}^{\dot{-}}$), benzoylacetate ($\text{Bzac}^{\dot{-}}$), and 2,6-dimethyl-3,5-heptanedionate ($\text{HDN}^{\dot{-}}$). The splitting constants of experimental spectra are analyzed by means of the INDO calculations with respect to possible stabilization of the anion radicals with various counterions.

EXPERIMENTAL

The experimental technique used was similar to that described in this Series. The reactions were carried out in argon atmosphere with exclusion of air and moisture directly in the EPR cells. The spectra were recorded and simulated with a Varian E-3 spectrometer connected to a Varian SS 100 computer. The beta diketones were obtained from the given sources or prepared by known procedures: Hacac (Lachema, Brno), HDPM (Fluka AG.), HBzac (ref.³), HHDN (ref.⁴). Their nickel salts were prepared as follows: Niacac₂ (ref.⁵), NiBzac₂ (ref.⁶), NiDPM₂ (ref.⁷), and NiHDN₂ (ref.⁷). The anion radicals of beta diketonates were obtained in the following way: *I*) $\text{acac}^{\dot{-}}$; 0.2 cm³ 0.2M-Niacac₂ in toluene was treated with 0.2 cm³ tetrahydrofuran and 0.08 cm³ 1.0M *n*-PrMgI in diethyl ether, *II*) $\text{Bzac}^{\dot{-}}$; 0.2 cm³ 0.1M-NiBzac₂ in benzene was treated with 0.2 cm³ 2M *n*-PrMgI in diethyl ether, *III*) $\text{DPM}^{\dot{-}}$; 0.2 cm³ 0.1M-NiDPM₂ in toluene was treated with 0.2 cm³ diisopropyl ether and 0.05 cm³ 2M *n*-PrMgI, *IV*) $\text{HDN}^{\dot{-}}$; analogous to *I*.

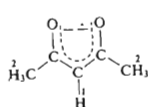
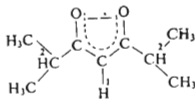
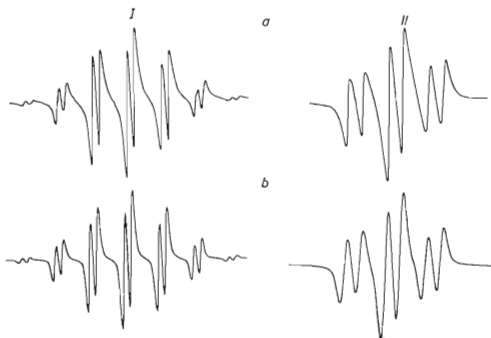
The calculations used the INDO method with original parametrization by Pople and coworkers⁸ differing partially from the parametrization by Kaufman⁹, which causes partial

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change of spin values as compared with those given in ref.¹. The parametrization by Clack and coworkers^{10,11} was used for the transition metal. The UHF method with partial annihilation of spin density¹² was adopted in the calculation. Standard geometry was considered for all the systems¹³.

RESULTS AND DISCUSSIONS

The experimental and simulated spectra of *I-IV* radicals are given in Fig. 1, and assignment of the splitting constants obtained by the simulation is presented in Table I. With respect to good resolution of hyperfine structure of the spectra and with respect to the number of splittings ($6 \cdot a_H = 1.25$ mT and $1 \cdot a_H = 0.26$ mT) as well as number of the protons in *I* radical, the assignment of the splitting constants to the protons of methyl group ($a_H = 1.25$ mT) and to methine proton ($a_H = 0.26$ mT) was unambiguous. Similar consideration applies also to structures *II* and *III*. By analogy with structures *I-III*, the splitting constants $a_H^1 = 0.245$ mT and $a_H^2 = 0.77$ mT were assigned to the methine proton and three equivalent methyl protons of structure *IV*, respectively. The remaining constants were assigned to the protons of aromatic nucleus in accordance with the generally known trend of spin density distribution

*I**II*

in benzene ring: the highest $a_H^p = 0.4$ mT to the *para* position, the next two to *ortho* positions ($a_H^o = 0.335$ mT and $a_H^o = 0.315$ mT), and the lowest $a_H^m = 0.11$ mT to the *meta* positions. The spectrum of structure *III* shows noteworthy ^{13}C satellite lines due to interaction of six equivalent carbon nuclei of methyl groups with the unpaired electron with splitting constant $a_{13c} = 0.63$ mT. The alkyl protons of Grignard reagents do not take part in formation of the hyperfine structure. The splitting constants and g -values ($g \approx 2.004_2$) of the spectra are practically unaffected by the kind of the Grignard reagent used (*i.e.* MeMgBr, EtMgBr, *n*-Pr-MgBr or PhMgBr). Also substitution of nickel by cobalt caused no change in hyperfine structure of the spectra.

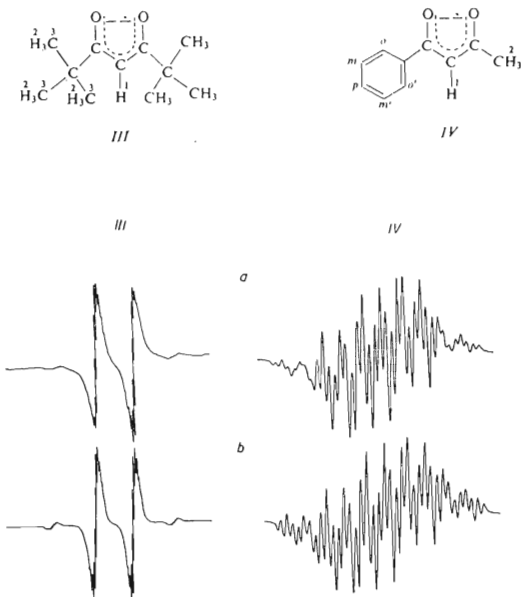


FIG. 1

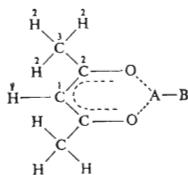
The experimental and simulated ESR spectra of the radicals observed in reactions of beta diketonates with Grignard reagents (a_H are the splitting constants, pp are half-widths of lines in mT *a* experimental, *b* simulated)

TABLE I
Assignment of splitting constants to anion radicals of beta diketonates

Structures	Splitting constants, mT		
	a_H^1	a_H^2	$a_{H,C-13}$
<i>I</i>	0.26	1.25	—
<i>II</i>	0.275	0.075	—
<i>III</i>	0.277	0.013	a_{C-13}^3 0.63
<i>IV</i>	0.245	0.77	a_H <i>o</i> 0.335 <i>o'</i> 0.315 <i>m</i> 0.11 <i>p</i> 0.4

TABLE II

s-Electronic spin densities for the structures: *a* $acac^{\cdot-}$, *b* $Liacac^{\cdot-}$, *c* $MgClacac^{\cdot-}$, *d* $NiCl_2acac^{\cdot-}$ (planar configuration), *e* $NiCl_2acac^{\cdot-}$ (tetrahedral configuration)



Atom	Structure				
	<i>a</i>	<i>b</i>	<i>c</i>	<i>d</i>	<i>e</i>
C^1	-0.00038	0.00013	0.0032	-0.00031	-0.00043
H^1	0.00701	0.00719	0.00315	-0.00061	-0.00656
C^2	0.00008	0.00055	0.00049	0.00007	0.00118
C^3	-0.0041	0.00003	0.00029	-0.00451	-0.00383
H^2	0.03506	0.00027	0.00055	0.02411	0.02438
O	0.00001	0.00592	0.02744	-0.00002	0.00216
A	—	0.72796	0.83348	-0.00001	-0.00002
B	—	—	0.04204	0.00000	-0.00022

The radical *I* was chosen as a model structure for the INDO calculations, taking into account possible counterions present in the system: *a*) the radical without counterion, *b*) with Li^+ , *c*) with MgCl^+ , *d*) with NiCl_2 (plane arrangement), *e*) with NiCl_2 (tetrahedral arrangement). The spin densities calculated for these structures and the values of splitting constants obtained therefrom are given in Tables II and III, resp. Heading of Table II shows the respective structure and numbering of the individual atoms.

The free acac^- itself is a π radical with predominant part of its spin density localized in p_z orbitals of carbon atoms lying in one plane. This fact is reflected by relatively high value of splitting constant of the methyl protons ($a_{\text{H}}^2 = 1.893$ mT) as compared with that of the methine proton ($a_{\text{H}}^1 = 0.378$ mT). In the case of coordination to Li^+ and MgCl^+ the spin density is redistributed, the original π -type radical acac^- being rearranged to σ radical. This change causes a strong increase of spin density of the methine proton and lowering of spin density of the methyl protons, which disagrees with experimental values ($a_{\text{H-Li}^+}^2 = 0.015$ mT, $a_{\text{H-Li}^+}^1 = 0.388$ mT, $a_{\text{H-MgCl}^+}^2 = 0.030$ mT, $a_{\text{H-MgCl}^+}^1 = 0.17$ mT). In the case of coordination to NiCl_2 the radical is of π -type, the spin density of methyl hydrogens being lowered practically to the experimental value due to delocalization of π electron density also to the NiCl_2 fragment ($a_{\text{H-planar}}^2 = 1.318$ mT, $a_{\text{H-tetrahedral}}^2 = 1.316$ mT, $a_{\text{H-experimental}}^2 = 1.25$ to 1.305 mT). As the radical is one of π type, plane configuration around the atom presents between conditions for transfer of the unpaired electron density to p_z orbitals of chlorine atoms as compared with the analogous compound in tetrahedral arrangement. As a consequence, the spin density at the methine proton is strongly lowered in the planar configuration as compared with that in the tetrahedral configuration ($a_{\text{H-planar}}^1 = 0.033$ mT, $a_{\text{H-tetrahedral}}^1 = 0.354$ mT, and $a_{\text{H-experimental}}^1 = 0.26$ – 0.425 mT). Energy balance shows, too, that the tetrahedral configuration around nickel is by 0.154 eV more favourable than the planar configuration.

TABLE III

The calculated splitting constants a_{H} of the structures *a*–*e* and the experimental values

Splitting constant	Structure					Experiment
	<i>a</i>	<i>b</i>	<i>c</i>	<i>d</i>	<i>e</i>	
a_{H}^1 (mT)	0.378	0.388	0.170	0.033	0.354	0.26–0.425
a_{H}^2 (mT)	1.893	0.015	0.030	1.318	1.316	1.25–1.305

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