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BRIDGED FERROCENES

VIII *. CORRELATION OF REDOX POTENTIALS WITH STRUCTURE

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Summary

The redox potentials for oxidation of ferrocenes with hydrocarbon bridges and of corresponding ketoferrocenes were measured. For the reduced compounds, correlations were observed between the potentials and the iron to ring distances. For the ketoferrocenes, the importance of proper alignment of the carbonyl with the cyclopentadienyl rings is noted. Other possible relationships are discussed.

Introduction

Since ferrocene and its derivatives undergo reversible oxidation by a variety of chemical and electrometrical techniques, a probe is available for the determination of the electronic effects of substituents. Many research groups have provided correlations of redox potentials with various properties of the substituents [1—21]. Relatively few investigations have been carried out on bridged ferrocenes [13,21]. Since various other properties of bridged ferrocenes had been observed that are correlated with structures peculiar to the bridges [21—28], it seemed appropriate to investigate the redox potentials of bridged ferrocenes extensively and to characterize similar correlations, if any.

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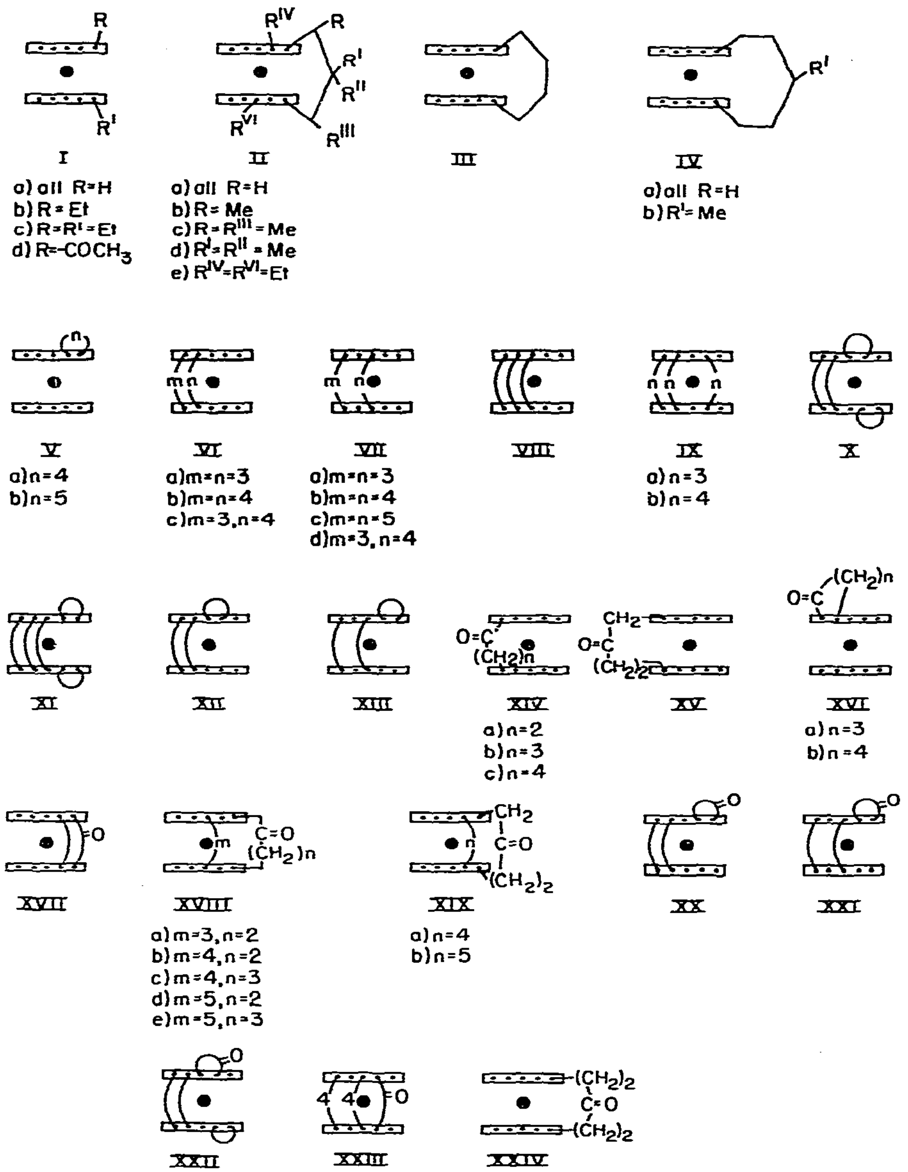

Fig. 1. Ferrocene derivatives. In each case the rectangles represent the cyclopentadienyl rings, the small solid circles the carbon atoms of the ring, the larger circles the iron atoms, and the arcs the bridges. The values for *n* and *m* are the numbers of the methylene groups in the bridges. The unlabeled arcs are trimethylene bridges. Unless otherwise noted, all R's are hydrogens.

Experimental

The experimental conditions for the cyclic voltammetry were the same as previously described [21]. α-Keto-1,1'-trimethyleneferrocene (XIVa) * (655

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* The structures of all of the compounds are in Fig. 1.

mV) or 1,1′,3,3′-bis(tetramethylene)ferrocene (VIIb) (265 mV) was used as an internal standard to eliminate systematic errors.

Ferrocene (Ia) and acetylferrocene (Id) were purchased from Arapahoe Chemicals. Samples of compounds Ib, Ic, IIb, IIc, IId, IIe, and IVb were generously contributed by Dr. T.E. Bitterwolf. All of the others were prepared by literature procedures [21—23,27—33]. All solid compounds were purified by recrystallization and/or chromatography, and the liquids by chromatography. Their purity was checked with IR spectra, by TLC, and, for some, by NMR.

Results

The potentials ($E_{1/2}$) of the ferrocene derivatives without carbonyl groups versus the saturated Ag/AgCl electrode are listed in Table 1. The potentials of the ketones are listed in Table 2. The column in Table 1 labeled $\Delta E_{1/2}$ lists the differences between the potential of ferrocene and those of the compounds. There are various other columns included in the tables that are used to aid in the interpretations of the data. They will be described during the discussion.

TABLE 1

REDOX POTENTIALS OF FERROCENE DERIVATIVES (mV)

	$E_{1/2}$	$\Delta E_{1/2}$ [a]	$\Delta E_{1/2}S$ [b]	$\Delta E_{1/2}C$ [c]	ΔQS [d]	ΔIS [e]	ΔD [f]
Ia	440	0	—	0	0	0	
Ib	383	57	57				
Ic	323	117	59				
IIa	367	73	37	24	0.111 (3)	0.024 (3)	2
IIb	372	68	34				
IIc	378	62	31				
IId	383	57	29				
IIe	255						
III	345	95	48	24	0.016 (5)	0.011 (3)	
IVa	296	144	72	29	0.023 (5)	0.002 (4)	
IVb	295	145	73				
Va	320	120	60				
Vb	309	131	66				
VIa	291	149	37	25	0.198 (3) [g]	0.047 (2) [g]	4
VIb	270	170	43	21	0.061 (3)	0.027 (3)	
VIc	275	165	41	23	0.154 (2)	0.041 (2)	
VIIa	358	82	21	14	0.347 (1)	0.102 (3)	6
VIIb	265	175	43	22	0.070 (3)	0.052 (3)	
VIIc	200	240	60	24	0.051(10) [g]	0.008(10) [g]	
VIId	268	172	43	25	0.131 (5)	0.047 (3)	
VIII	270	170	28	19	0.128(10)	0.039(10)	
IXa	363	77	13	9	0.542 (3)	0.172 (2)	9
IXb	183	257	43	21	0.105 (6) [g]	0.057 (4) [g]	2
X	77	363	45 [h]		0.234 (2)	0.088 (3)	4
XI	27	413	41 [h]				6
XII	172	268	45 [h]		0.203 (4) [g]	0.055 (4) [g]	4
XIII	245	195	33 [h]		0.313 (2) [g]	0.111 (2) [g]	6

[a] $E_{1/2}$(ferrocene) — $E_{1/2}$(compound). [b] $\Delta E_{1/2}$/number of substituents on cyclopentadienyl rings. [c] $\Delta E_{1/2}$/number of methylenes in bridges. [d] QS(ferrocene) — QS(compound) (from Ref. 26, except where noted) in cm/sec. [e] IS(ferrocene) — IS(compound) (from Ref. 26, except where noted) in cm/sec. [f] Fe—ring distance (ferrocene) — Fe—ring distance (compound) in pm. [g] New results. [h] Corrected $\Delta E_{1/2}$/S: X, 33; XI, 31; XII, 38; XIII, 20.

TABLE 2

REDOX POTENTIALS OF KETOFERROCENES (mV)

	$E_{1/2}$	ΔV	$E_{1/2}$	ΔV	
Id	681	298	XVIIIc	588	323
Ie	902	290	XVIIId	496	
XIVa	655	288	XVIIIe	516	
XIVb	655	310	XIXa	408	143
XIVc	640	344	XIXb	354	
XV	495	150	XX	537	365
XVIa	640	320	XXI	576	331
XVIb	602	293	XXII	471	394
XVII	510	219	XXIII	462	
XVIIIa	660	302	XXIV	453	70
XVIIIb	563	295			

[a] [E(ketone) — E(corresponding hydrocarbon)]/number of carbonyls.

In agreement with the literature [21,34], the potential of ferrocene was found to be 440 mV versus sat. Ag/AgCl at a Pt electrode in a solution 0.1 F in n-Bu_4NClO_4 in CH_3CN.

Discussion

The sensitivity of the potential to the electronic effects of the substituents on the cyclopentadienyl rings have been well studied [1—13,19,21], and the additivity of the polar effects of these substituents has been discussed [13,19]. The effect of alkyl substitution on the ring can be deduced directly from the potentials of simply substituted ferrocenes such as Ib and Ic by subtracting the potential of ferrocene and from the potential of the ring alkylated bridged ferrocene, IIe, by subtracting the potential of the corresponding unalkylated bridged compound, IIa. In this way, the effect of an alkyl group is to reduce the redox potential of ferrocene by 57(1) mV.

A compound with a single homoannular trimethylene group is unknown, but the contribution of the homoannular trimethylene group may be assessed by a similar technique. In the four compounds available (X, XI, XII, and XIII) subtraction of the contribution of the rest of the substituents, as obtained from compounds having only those substituents (VIa, VIII, VIa, and VIIa, respectively), leaves the contribution of the homoannular trimethylene group or groups. The results per homoannular group then become 107, 122, 119, and 112 mV, respectively, which are reasonably constant and average to 115(3) mV. Since each homoannular group is a double substituent, the contribution per substituent is 57(2) mV, the same as for the alkyl group.

When applying the additivity property to the results for the heteroannular compounds studied in the present work, it is immediately clear that the contribution of each substituent is not the same. The range, given in the column labeled $\Delta E_{1/2}/S$, is 13 to 74 mV and not 57 mV as expected from the results obtained from ring alkyl and homoannular substitution. Thus, other effects besides the additive polar effect must be inforce.

Factors that we will consider below include 1) polarization effects of the solvent, 2) steric effects of the bridges blocking the iron from the electrode, 3) hyperconjugation of the α-methylenes with the cyclopentadienyl rings, 4) inductive effect of the entire bridge by direct interaction with the iron, and 5) iron to ring distances.

The solvent used in all of these measurements was acetonitrile which is known to be a weakly polarizing solvent. Furthermore, as will be discussed below, correlations were obtained between the redox potentials and crystallographic and Moessbauer parameters. For the parameters obtained in the solid state to reflect the same effect as polarization by the solvent must involve a high degree of coincidence.

Gorton et al. [13] have discussed the possibility that shielding of the iron atom by a bridge might prevent the interaction of the iron with the electrode, thus preventing the removal of an electron from the iron and decreasing the ease of oxidation. They note that this phenomenon did not obtain when comparing IVa with Ia. There have been several other reports concerning the interaction of the iron atom as a requirement for reaction, most recently in the hydrogenation studies [27] and in the protonation of ferrocene in strong acids [35]. Whether or not the reaction proceeds through an intermediate iron complex, the initial and final states are not affected, and the potentials, as thermodynamic functions, are also unaffected. Steric hindrance of the iron will, on the other hand, affect the kinetics of the electrode reaction. We noted no evidence for this and draw no conclusions concerning the participation of the iron atom.

The greater hyperconjugative donation of electron density to the cyclopentadienyl rings has been suggested as a mechanism for the greater ease of oxidation of IVa than III and IIa [13]. We offer three counterarguments. Models suggest that the orientation of the C—H bonds on the α-methylenes of IVa are not significantly different from those of III and IIa. Substitution of the *exo*-α-protons (this configuration was established by means of NMR) of IIa with methyl groups to form IIb and IIc increases the potentials by 5 and 11 mV, respectively, significantly less than the 22 and 71 mV differences observed for IIa, III, and IVa. Finally, for compounds IIa, VIa, VIIa, VIII, and IXa, which have only trimethylene bridges, the effect of hyperconjugation is expected to be the same for each bridge. Yet, the contribution per bridge varies from 25 mV to 75 mV (or 13—37 mV per substituent). The effect of hyperconjugation is, therefore, estimated to be small and does not account for the major effects of the bridges.

There are also small differences among the contributions of the homoannular tri-, tetra- and pentamethylene groups. These differences may also be attributed to hyperconjugation, whereby the more flexible pentamethylene is capable of proper alignment with the cyclopentadienyl rings.

Another possible consideration is that the entire bridge is affecting the potentials, the α-methylenes by interaction with the cyclopentadienyl rings, and the other methylenes by direct interaction with the iron. Direct interaction of substituents with the iron has been considered often; however, no incontrovertible substantiation of such an interaction has been offered. The argument is, at first, supportable here by noting that, except for VIIa, VIII, and IXa, the change in potential per methylene group is essentially constant for all bridged compounds without substituents on the bridges. These results are tabulated in Table 1 in the

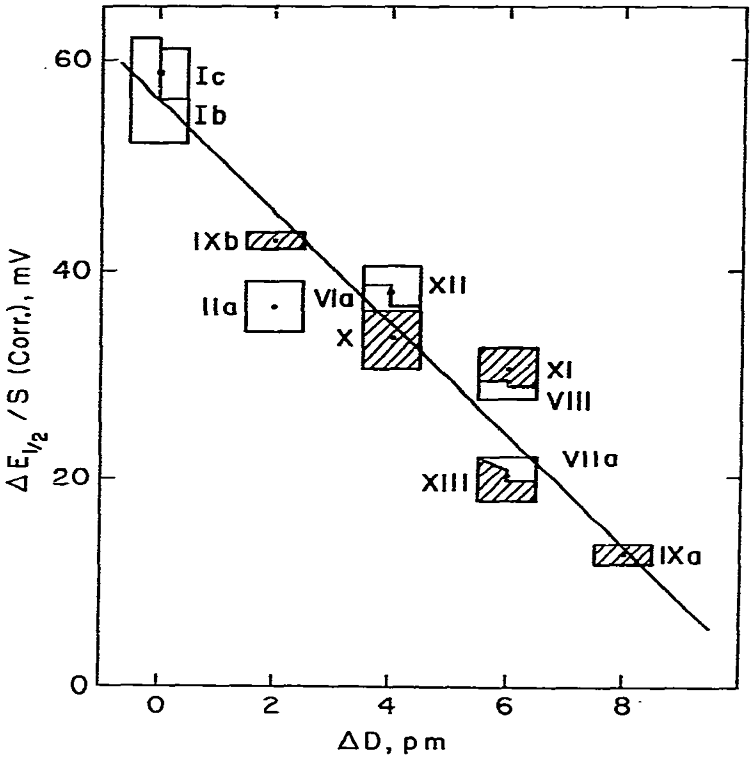

Fig. 2. Correlation of changes in potentials with changes in iron to ring distances.

column labeled $\Delta E_{1/2}/C$. Since substitution of bridge protons by methyl groups (IIb, IIc, IId and IVb) gives a very small change in the potential, the effect, if it exists, is inductive and does not involve the overlap of C—H bond orbitals with the iron orbitals. The contributions of the bridges should, however, be greater than observed since they would come from the combination of inductive effects, that of the α-methylenes through the cyclopentadienyl rings and that of all of the other methylenes through the iron.

The fifth item for consideration concerns the iron to ring distances of the compounds. The iron to ring distances have been shown [26] to be correlated with the Moessbauer parameters. Squeezing the iron atom increases both the electron density around the iron and causes the electronic environment to become more oblate. These changes in the electronic environment in turn decrease the inductive effect of the substituents and yield higer potentials than otherwise expected.

Crystal structures have been determined for seven (Ia, VIIa, IXa, IXb, X, XI, and XIII) of these compounds studied [36—42, and 27, respectively] and for one ketoferrocene (XIVa) [43]. For others, the iron to ring distances are estimated to be the same as those with the same number and arrangement of bridges (XIVa for IIa, Ia for Ib and Ic, X for VIa and XII, XI for VIII, and XIII for VIIa). A comparison of the changes in iron to ring distances (from that in ferrocene) versus the changes in redox potentials (from that of ferrocene) per

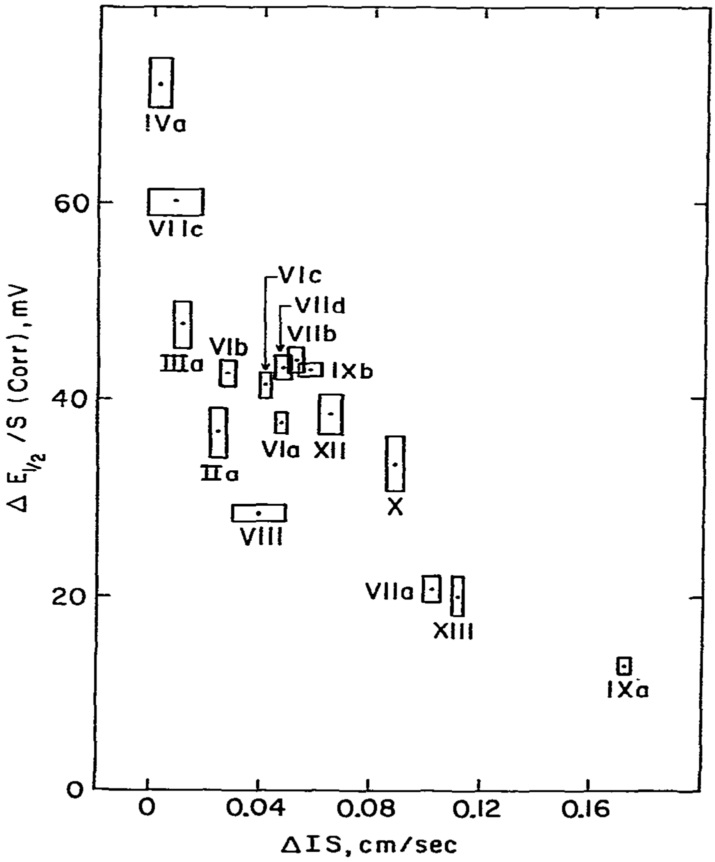

Fig. 3. Correlation of changes in potentials with changes in isomer shifts.

substituent (after subtracting the contributions of the unaffected * homotrimethylenes) is given in Fig. 2. A reasonable correlation is observed. Since a correlation had been observed between the distances and the Moessbauer parameters, as noted above, then the correlation should also exist between the potentials and the Moessbauer parameters (which are available for more compounds than are crystal structures). Figures 3 and 4 illustrate the correlations for the isomer shifts and for the quadrupole splittings, respectively.

Even though the correlation between the iron to ring distances and the potentials appears to be linear, there is no a priori reason to expect this. The correlations between the Moessbauer parameters and the potentials do not appear to be linear unless compounds IVa and VIIc are excluded. Both of these differ from the rest by having pentamethylene bridges. Unusual results have been noted earlier [28] for chemical and physical properties of compounds with pentamethylene groups.

The major question that remains from the above analysis is why the bridged

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* Since the contribution of the homoannular trimethylene group is constant for all such compounds, it is apparent that there is no effect by the changes in iron to ring distances on the contributions.

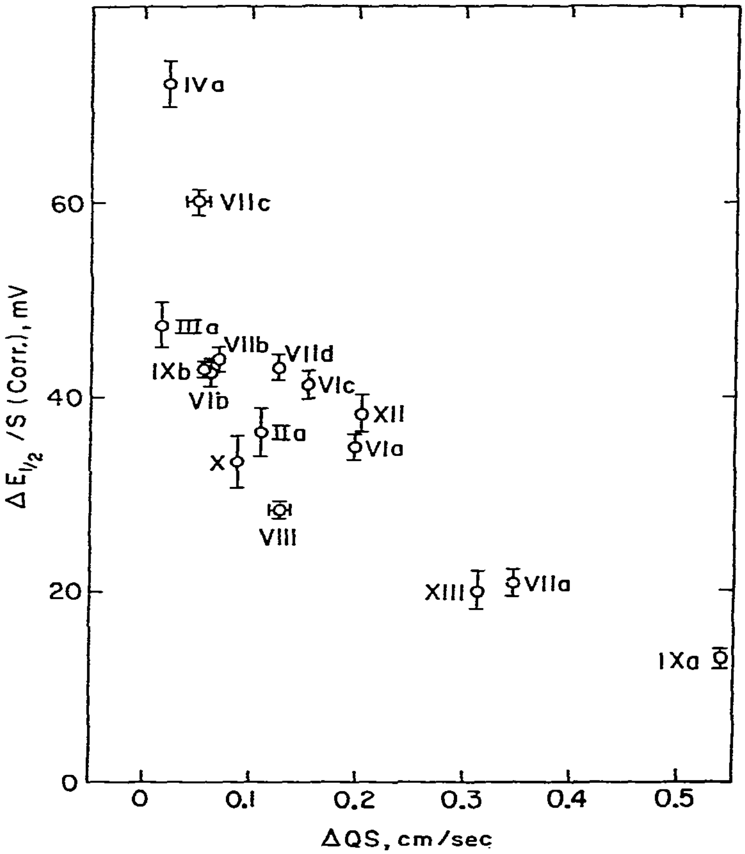

Fig. 4. Correlation of changes in potentials with changes in quadrupole splittings.

polymethylenes should be affected by the iron to ring distances while the homoannular polymethylenes are not. A possible explanation lies with the oblateness of the electron gradient on the iron atom [44]. With the decreased iron to ring distances, the increasingly oblate electron field interacts with the bridge but not the homoannular and other nonbridging groups. This implies that the entire bridge may be involved in the inductive effect. However, the equal contribution of each methylene group as discussed above remains in question. After subtraction of the effect of the iron to ring distances, except for the pentamethylene bridges, the differences are small and the errors are too large for any conclusions to be drawn.

Gorton et al. [13] discuss the effect of having an α-keto group on the bridge. In accord with cited electronic spectra, the contribution of the carbonyl depends on the ability to align with the cyclopentadienyl rings to maximize conjugation. These authors compared the potentials directly and did not consider the different contributions of the bridges without the carbonyls. The results we have obtained for the relative potentials differ from theirs, possibly because of the differing solvents, and our potentials do not comply with their interpretation. However, when accounting for the contributions of the bridge without the ketone, our results fall into accord with their interpretation. This is indicated in Table 2 where the column labeled ΔV is the difference between the reduced derivative and the ketoderivative. The results for the ketotrimethylenes (excluding the out-of-line value for XVII) average to 295(4), the ketotetramethylenes to 316(7), and the single pentamethylene is 344 mV. The contribution of the carbonyl in XVII is probably as low because steric interference of the adjacent bridge prevents the carbonyl from proper alignment.

The results for the homoannular derivatives (XVIa, XVIb, XX, XXI, and XXII) can be similarly interpreted. Here, however, the situation is reversed. The contribution of the carbonyl is smallest in the ketopentamethylene and largest in the ketotrimethylene (avg. 363(18)). The rigidity of the ketotrimethylene forces the group to be coplanar with the cyclopentadienyl ring, while the increased flexibility of the other two allows them to achieve other conformations. Conformations with increasingly noncoplanar carbonyls become energetically attractive to avoid unfavorable torsion angles of adjacent C—H bonds.

Even when the carbonyl is not conjugated with the cyclopentadienyl ring, there remains an electron-withdrawing effect, increasing the redox potentials (147(4) mV for compounds XV and XIXa, Table 2, and 70 mV for XXIV in 90% ethanol [13]). Although the effect of the β-carbonyls may be explainable by a form of homoconjugation or by invoking "enolic" resonance forms, the effect of the γ-carbonyl, XXIV, cannot be so explained. An explanation has been offered [13] that the effect in XXIV may be due to the field of the iron atom. This may also be true to some extent for the β-carbonyls.

A resolution of the several questions raised probably requires the determination of the crystal structures for a much larger selection of compounds.

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