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RADICAL ADDUCTS OF DIBENZOFULVENES AND 9-METHYLENANTHRONE - AN ESR STUDY

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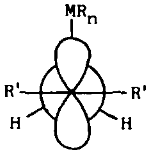
Abstract - The title compounds were reacted with a series of $R_3M\cdot$ radicals ($M = C, Si, Ge, Sn, P, O, S$) to give the corresponding paramagnetic adducts. In the case of 9-methylenanthrone radical addition occurred selectively at the exocyclic carbon-carbon double bond even with Group IV B organometallic radicals for which attack at the carbonyl oxygen would give rise to thermodynamically more stable adducts. When irradiating solutions of 9-methylenanthrone a photoinduced self-reaction leading to the formation of dimeric species took place. On the basis of the measured ESR spectral parameters the structure of the adducts is discussed, as well as the influence of the R_nM groups on the β-proton hyperfine splitting constants.

The magnitude of the β-proton hyperfine splitting constants in β-substituted ethyl radicals $R'_2\dot{C}-CH_2MR_n$ is commonly related to the preferred conformation by means of equation (1)

$$\underline{a}(H_\beta)=B\langle\cos^2\theta\rangle, \qquad (1)$$

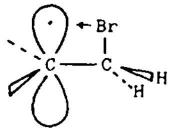
where θ is the dihedral angle between the symmetry axis of the $2p_z$ orbital on C_α and the C_β-H_β bond, and B is assumed to be a constant.[1] According to eqn (1), in a conformation like (A) where the MR_n group eclipses the $2p_z$ orbital on the radical carbon centre, $\underline{a}(H_\beta)$ should be equal to B/4 and independent of the nature of the substituent.



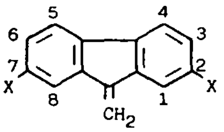
(A)

This prediction can be tested by choosing ethyl radicals containing R' substituents on C_α bulky enough to compel the MR_n group in conformation (A). In practice it has been found that $\underline{a}(H_\beta)$ is far from being a constant as its value varies by as much as a factor of 2 depending on MR_n.[2-8] Actually, by changing the leading atom M of the substituent within the first row, the β-proton splitting remains reasonably constant and its average value $\bar{\underline{a}}(H_\beta)$ is generally found to be somewhat greater than B/4.[9] On the other hand, with second or higher row substituents, values larger than $\bar{\underline{a}}(H_\beta)_{\underline{\text{row I}}}$ are found for SiR_3, GeR_3, SnR_3 and PL_n groups[2,3,6,7,9] and smaller than $\bar{\underline{a}}(H_\beta)_{\underline{\text{row I}}}$ for SR,[2,7] Cl[3,5,9,10] and Br[8]. These anomalies are usually explained in terms either of: i) variations in the electron-releasing power of the C_β-H_β bond towards the singly occupied orbital due to the differences in the electronegativities of the MR_n substituent,[11] i.e. to the non-constancy of the B term; or of ii) distorsions of the molecular skeleton causing the substituent to move towards the radical centre and the β-protons away from it with a consequent decrease of $a(\mathrm{H}_\beta)$ ("bridging hypothesis"),[2,5,10] or vice versa.[6]

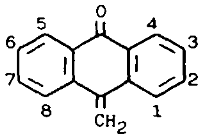
Definite experimental evidence in favour of the latter interpretation has never been obtained. Only in the case of β-bromoethyls the ESR results suggest that the radical "has moved towards the bridging structure (B) without being symmetrically bridged".[12] As far as other substituents are concerned, we have examined in two previous investigations a large number of radical adducts of 1,1-diphenylethylene[9] and of para-substituted 1,1-diphenylethylenes[13] and we have found that neither of these two interpretations explains satisfactorily the experimental data. An inadequacy of 1,1-diphenylethyls is however the non-rigidity of the molecular skeleton which causes small departure of these radicals from a perfectly eclipsed geometry. The variations of the $a(\mathrm{H}_\beta)$ splitting may therefore partially arise from differences in the minimum energy geometry adopted by the variously substituted 1,1-diphenylethyls.


(B)

Related but more suitable derivatives for similar investigations are 9-methylenfluorene (**Ia**) and 9-methylenanthrone (**II**) which, being more rigid and planar than 1,1-diphenylethylene because of the presence of the additional cycle, will afford radical adducts which are more likely to be found in the eclipsed conformation (A).



(**Ia**); X=H
(**Ib**); X=Bu^t



(**II**)

We report here an ESR study on the radicals obtained from these two derivatives and from 2,7-di-tert-butyl-9-methylenfluorene (**Ib**).

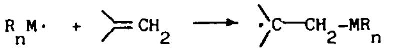
EXPERIMENTAL

9-Methylenanthrone[14] and 9-methylenfluorene[15] were prepared according to the literature.

The ^{1}H-N.M.R. spectra were recorded with a Varian EM 360L instrument using tetramethylsilane as an internal standard; mass spectra were performed with a Jeol JMS-D100 spectrometer at an ionization energy of 70 eV.

2,7-Di-tert-butyl-9-methylenfluorene (**Ib**). To an ethereal Grignard solution from methyl iodide (1.70 g, 12 mmol) and magnesium (0.30 g, 12 mmol), 2,7-di-tert-butylfluorenone[16] (3.20 g, 11 mmol) in dry diethyl ether (100 ml) was added dropwise. The reaction was kept at room temperature for 30 min and then refluxed for 1 h. After cooling the mixture was carefully hydrolized with an aqueous ammonium chloride solution; the organic layer was separated and dried ($MgSO_4$) and the solvent was removed under vacuum. The residue was treated with 1,4-dioxane and then refluxed with 20% sulphuric acid (10 ml) for 1 h. The mixture was poured into ice-water and extracted twice with diethyl ether. The organic phase was dried ($MgSO_4$) and the solvent was removed under reduced pressure. The residue was chromatographed on silica gel (Kieselgel 60, 70-230 mesh ASTM, Merck) by elution with light petroleum (40-70) to give the title compound (2.4 g, 75%), m.p. 170-172°C (from light petroleum); ^{1}H-NMR ($CDCl_3$) δ 1.4 (18H, s), 5.95 (2H, s) and 7.20-7.80 (6H, m); MS (m/z): 290 (M^+, 30), 275 (100), 245 (17), 102 (85), 57 (96). (Found: C, 91.38; H, 8.98%. Calc. for $C_{22}H_{26}$ C, 91.05; H, 8.95%).

The radical adducts were generated in deoxygenated benzene or tert-butylbenzene solutions by reacting photolytically produced $R_nM\cdot$ radicals with the appropriate alkene according to eqn (2).



$$R_nM\cdot + \rangle\!\!=\!CH_2 \longrightarrow \rangle\!\dot{C}-CH_2-MR_n \qquad (2)$$

The methods used for generating the transient $R_nM\cdot$ radicals have been described in the previous papers.[9,13]

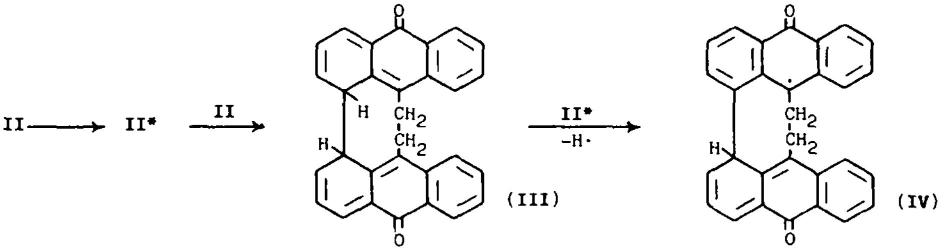
Well-resolved ESR spectra of the adducts of 9-methylenanthrone could be obtained at or near to room temperature, while with the methylenfluorenes (**Ia**) and (**Ib**) spectra strong enough to be interpreted were observed with some exceptions at higher temperatures.

The radical adducts of (**Ia**) showed very complex hyperfine splitting patterns, so that we preferred to use more extensively its di-*tert*-butyl substituted derivative (**Ib**) which provided simpler spectra and stronger signals.

Disappointingly, in no case could we obtain chlorine adducts of the three investigated olefins.

RESULTS AND DISCUSSION

General remarks. The reaction of $R_nM\cdot$ radicals with (**Ia**), (**Ib**) or (**II**) usually gave clean ESR spectra of the expected adducts. An exception to this behaviour was found when using 9-methylenanthrone as substrate, since in some cases the spectrum of the adduct of (**II**) was accompanied by that of a second species consisting of a doublet (separated by 31.07 G) of multiplets (*a*(2H) 0.81, *a*(2H) 0.98, *a*(1H) 3.20, *a*(2H) 3.44, *a*(2H) 0.33 G, *g* 2.0033 in benzene at 298 K). A neat spectrum of the latter species could be observed by irradiating solutions of (**II**) without any reactant. By cooling down the solution new broad lines appeared in the central part of the spectrum which became sharper the lower was the temperature. Eventually, at 228 K in toluene, the spectrum consisted of a doublet (a_H = 22.68 G) of doublets (a_H = 8.48 G) of multiplets. On the basis of the measured couplings we attribute this spectrum to radical (**IV**) formed *via* the mechanism showed in Scheme 1 involving initial U.V. excitation of 9-methylenanthrone to its triplet state followed by attack to an unexcited molecule to give the dimer (**III**); hydrogen abstraction from the latter by a second triplet molecule eventually affords the observed radical (**IV**).



Scheme 1

The hyperfine pattern is in fact consistent with a radical arising from a methylenanthrone substituted at position 1 (one of couplings of *ca* 3 G is missing) and having a $-CH_2-CH_2-$ attached to the radical centre, as indicated by the 0.33 G triplet splitting. Moreover, the values of $a(H_\beta)$ (22.68 and 8.48 G) from which angles for the two β-protons of *ca* 8 and 128 degrees can be derived,* suggests that some constraint (the presence of the eight membered ring) forces these protons quite far from the equilibrium conformation (θ=60°) of the other adducts of (**II**). The selective line broadening effect observed above 230 K can also be explained in terms of structure (**IV**) as arising from modulation of the β-proton splittings produced by ring motions. Finally, the mechanism of Scheme 1 is supported also by mass spectral analysis of the reaction mixture which shows a peak with m/z=412 corresponding to the molecular weight of the dimer (**III**).

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* The angle θ can be calculated from the ratio $a(H_{\beta,1})/(a(H_{\beta,2}) = \cos^2\theta/\cos^2(\theta+120)$ which results from eqn (1) if torsional effects are neglected.

A further point worth of comment is the behaviour of 9-methylenanthrone when reacted with silicon, germanium and tin centred radicals. Due to the presence of two reactive sites, i.e. the exocyclic C=C and C=O double bonds, in principle attack may occur at either of these. On thermodynamic basis the addition of silyl or germyl radicals to the carbonyl oxygen should be more exothermic than addition to the methylene carbon when considering the difference in strength of the bonds being broken, i.e. C=O and C=C (76 and 60 Kcal mol^{-1}, respectively) and of the bonds being formed, i.e. O-Si and C-Si (from 108 to 128 Kcal mol^{-1}, and 89 Kcal mol^{-1} respectively).[17] However when reacting these radicals with (II) at room temperature, only adducts arising from attack at the methylene carbon are observed. At 400 K a second spectrum attributable to the organometallic adduct of 9,10-anthraquinone becomes also detectable. Triphenyl stannyl radicals, $Ph_3Sn^{\cdot}$, behave similarly although the spectrum of the carbon adduct observed at room temperature is much weaker than those of the silicon and germanium analogues, while in the reaction of (II) with $Bu_3Sn^{\cdot}$ and $Me_3Sn^{\cdot}$ the anthraquinone adducts were the only observable radical species.

The preferential formation of carbon adducts with respect to the thermodynamically more stable oxygen adducts indicates that the addition of silicon and germanium centred radicals and of $Ph_3Sn^{\cdot}$ to methylenanthrone is kinetically controlled.

The detection at high temperature of the organometallic adducts of anthraquinone is not easily explained. Since anthraquinone was not present in the sample, even in trace amounts, its formation might be due to photoinduced autooxidation of methylenanthrone; radical attack on the quinone will then lead to the observed adduct.

Effects of the substituent on the β-proton splitting. An examination of Table 1 shows that the $a(H_\beta)$ splitting for the adducts of first row radicals with the methylenfluorenes and methylenanthrone are reasonably constant, their average values, i.e. 7.54 and 6.26 G for the adducts of (I) and (II) respectively, being remarkably lower than in the corresponding β-substituted 1,1-diphenylethyl radicals (9.35 G).[9] To establish whether this difference is due to electronic or conformational factors we need to know what value of $a(H_\beta)$ would be predicted by eqn (1) in the eclipsed conformation of the presently investigated radicals. To this purpose the constant B is required. For a given substituted ethyl $R_2\dot{C}\text{-}CH_2X$, B is usually taken as twice the hyperfine splitting at the methyl protons in the related $R_2\dot{C}\text{-}CH_3$ radical, where $\langle\cos^2\theta\rangle$ is 0.5.[9] However we are not aware of any ESR study of either 9-methylfluorenyl or 9-methylanthronyl, even though ESR data have been reported for 9-fluorenyl and anthronyl where $a(H_9)$ is 13.9[18] and 12.0 G[19] respectively. These values are smaller than the related $a(H_1)$ splitting of diphenylmethyl (14.7 G)[20] thus reflecting a lower spin density on the radical carbon centre. Since also B varies linearly with spin density, values of 29.5 and 25.4 G may be derived for the adducts of (I) and (II), respectively, from the knowledge of B in 1,1-diphenylethyls (31.2 G).[9] According to eqn (1), in the eclipsed conformation of these radicals $a(H_\beta)$ is expected to be 7.37 and 6.35 G, respectively, in very good agreement with experiment as far as first row substituents are concerned. This behaviour contrasts with that of 1,1-diphenylethyls where $\bar{a}(H_\beta)_{\text{row I}}$ (9.35 G) was found to be much greater than the predicted value (7.8 G).[9]

We suggest that in the adducts of (I) and (II) the matching between experiments and predictions is due to the fact that not only the minimum energy conformation corresponds to perfect eclipsing of the β-substituent with the $2p_z$ orbital on C_α, but also torsional oscillations about the equilibrium position are small, while in 1,1-diphenylethyls neither of these conditions is thourougly fulfilled. In further support to this explanation it can be added that, at variance with diphenylethyls,[9] no linewidth alternation effects have been observed in the ESR spectra of the adducts of (I) and (II), the only exception being the diphenylphosphinyl adduct of methylenanthrone below room temperature.

It seems therefore that the presently studied radicals are better substrates than those so far investigated to check the electronic and structural factors controlling the magnitude of the β-proton hyperfine splitting constants in the absence of conformational effects.

In the light of the above considerations, the most remarkable feature emerging from the data of Table 1 is that ethyl radicals containing β-thiyl substituents shows β-proton splittings which are similar or only slightly lower than those containing first row substituents. In 1,1-diphenylethyls and in several other dialkylethyls where sterical constraint is not so strong as in the adducts of (I) or (II) the low values of $\underline{a}(H_\beta)$ observed for R_nM = SR have in our opinion to be attributed mostly to the fact that the thiyl group is more tightly held in the eclipsed conformation than first row substituents. This is in line with the well known ability of elements of rows higher than 1 to adopt conformation (A) even in the absence of crowding around the radical centre.[2-6]

A second point, which has never been much emphasized before, is that the most anomalous behaviour, as far as the magnitude of the β-proton splittings is concerned, is experienced by the radical adducts of Group IVB and VB substituents as SiR_3, GeR_3, SnR_3 and PL_n. In fact, the higher than expected $\underline{a}(H_\beta)$ couplings can not be attributed to departure from the eclipsed geometry for the reasons discussed above, and therefore must be due to some intrinsic property of these elements. Since, at present, any consideration of the origin of this behaviour would be only speculative, we prefer not to further argue about this point.

ACKNOWLEDGEMENT

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Table 1. Hyperfine splitting constants (Gauss = 10^{-4} Tesla) and g-values for the radical adducts of (Ia), (Ib) in tert-butylbenzene and of (II) in benzene.

Substrate	MR_n	$a_{H\beta}$	a_H (ring)	a_{MR_n}	g	T/K
(Ia)	Bu^t	7.60	3.65, 0.80[a]	-	2.0025	373
	CMe_2CN	7.40	3.65, 0.80	-	"	"
	OEt	7.70	3.59, 0.76	-	"	"
	$SiPh_3$	10.09	3.52, 0.76	-	"	"
	$GePh_3$	9.51	3.50, 0.75	-	2.0026	"
	SPh	7.84	3.56, 0.76	-	2.0028	"
(Ib)	Me	7.65	3.62, 0.73[b]	-	2.0025	298
	Bu	7.60	3.60, 0.72	-	"	378
	1-Ad	7.68	3.59, 0.71	-	"	388
	Ph	7.86	3.62, 0.72	-	"	398
	CMe_2CN	7.37	3.69, 0.69	-	"	378
	CF_3	7.53	3.78, 0.60	0.60(3F)	2.0026	298
	CCl_3	6.88	3.72, 0.66	-	2.0030	386
	OEt	7.72	3.64, 0.73	-	2.0024	395
	$SiPh_3$	10.02	3.52, 0.72	-	2.0025	398
	$GePh_3$	9.35	3.47, 0.70	-	2.0026	368
	$SnPh_3$	9.29	3.35, 0.69	-	2.0022	298
	$P(O)(OEt)_2$	8.97	3.63, 0.61	58.77(^{31}P)	2.0026	"
	SMe	7.70	3.65, 0.60	0.32(3H)	2.0027	"
	SPh	7.35	3.59, 0.63	-	2.0027	"
(II)	Me	5.98	2.92, 0.85, 3.28, 1.01[c]	0.22(3H)	2.0034	333
	Bu	6.57	2.92, 0.81, 3.28, 0.98	0.17(9H)	2.0033	298
	1-Ad	6.65	2.91, 0.90, 3.28, 0.90	-	2.0034	"
	Ph	6.32	2.98, 0.83, 3.33, 1.01	0.17(2H)	2.0034	"
	CMe_2CN	6.18	2.95, 0.82, 3.35, 1.00	0.13(6H)	2.0033_5	"
	C(O)Ph	6.46	2.99, 0.80, 3.33, 1.00	-	2.0033	328
	CF_3	6.10	3.09, 0.83, 3.46, 1.06	0.61(3F)	2.0039_2	298
	CCl_3	5.94	3.06, 0.78, 3.39, 1.08	-	2.0037	"
	OEt	6.16	3.01, 0.87, 3.39, 1.05	0.18(5H)	2.0033_3	355
	$SiPh_3$	8.55	2.80, 0.88, 3.15, 0.88	-	2.0033_6	298
	$GePh_3$	8.05	2.75, 0.87, 3.10, 0.87	-	2.0034_7	"
	$SnPh_3$	8.04	2.65, 0.86, 2.99, 0.86	-	2.00297	"
	PPh_2	7.66	2.88, 0.90, 3.27, 0.90	21.07(^{31}P)	2.00359	"
	$P(O)(OEt)_2$	7.43	2.97, 0.82, 3.33, 1.02	51.15(^{31}P)	2.0034_4	"
	$P(S)(OEt)_2$	7.34	2.96, 0.78, 3.28, 1.02	40.09(^{31}P)	2.00326	"
	SMe	5.74	2.95, 0.83, 3.32, 1.01	0.36(3H)	2.0037	"
	SEt	5.79	2.92, 0.83, 3.31, 1.02	0.41(2H) 0.19(3H)	2.0037	308
	SPh	5.53	2.96, 0.80, 3.29, 1.03	-	2.0036_4	298

[a] In the order $a_1=a_3=a_6=a_8$, $a_2=a_4=a_5=a_7$

[b] In the order $a_1=a_3=a_6=a_8$, $a_4=a_5$

[c] In the order $a_1=a_8$, $a_2=a_7$, $a_3=a_6$, $a_4=a_5$. The assignment of the hfs constants at protons 2,7 and 4,5 might be reversed.