Sterically Hindered Free Radicals. Part 20.[1] EPR and ENDOR Spectroscopy of α-Carbonyl Radicals

Bernd Kubiak,[a] Manfred Lehnig,*,[a] Wilhelm P. Neumann,[a] Ursula Pentling[a] and Antonios K. Zarkadis[b]
[a] *Lehrstuhl für Organische Chemie I, Universität Dortmund, Otto-Hahn-Str. 6, D-4600 Dortmund 50, Germany*
[b] *Section of Organic Chemistry and Biochemistry, University of Ioannina, 45110 Ioannina, Greece*

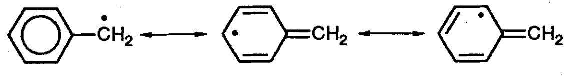
The hyperfine coupling constants and *g* values of 11 α-carbonyl radicals $^{\bullet}CR^1R^2(CRO)$ (**1**) and $^{\bullet}CR^3(CN)(CRO)$ (**2**) (R = H, Me, Ph, α-Naph; R^1, R^2, R^3 = H, CO_2Et, Ph, 2,4-Me_2Ph, Mes) have been determined by EPR and, partially, ENDOR spectroscopy. The *g* values lie between 2.0025 and 2.0051. Except for $^{\bullet}CH(CO_2Et)(CMeO)$, the *g* values are smaller than expected because of the steric hindrance of the substituents R^1, R^2 and R^3. The CRO group is twisted out of the nodal plane of the radical which diminishes the delocalisation of the unpaired electron over the carboxyl group. The proton splittings in the α-aryl substituents differ significantly from those found in $^{\bullet}CH_2Ph$ because of distortions. Proton splittings in benzoyl groups have been observed for the first time.

α-Carbonyl radicals $^{\bullet}CH_2CRO$ (R = H, Me, Ph) are characterized by relatively high *g* values (*ca.* 2.004)[2–5] which is explained by delocalisation of the unpaired electron over the carbonyl group.[6,7]


(1)

A fixed planar conformation is adopted which perturbs the unpaired electron by the comparatively high spin orbit coupling of oxygen. In contrast, the *g* value of $^{\bullet}C(Bu^t)_2[C(CF_3)O]$ falls to that expected for *tert*-butylmethyl radicals (2.0028).[8] This is explained by twisting the CRO group through 90° which prevents delocalisation of the unpaired electron onto oxygen.

It is known from phenyl-substituted radicals that steric hindrance has an analogous consequence. It disturbs the delocalisation of the unpaired electron into the phenyl group by twisting the phenyl ring out of the nodal plane. Because of this, the *o* and *p* splittings are markedly lowered.[9,10]


(2)

We present the hf data of substituted α-carbonyl radicals $^{\bullet}CR^1R^2(CRO)$ (**1a–f**) and $^{\bullet}CR^3(CN)(CRO)$ (**2**) (R = H, Me, Ph, α-Naph; R^1, R^2, R^3 = H, CO_2Et, Ph, 2,4-Me_2Ph, Mes) and discuss their influence on the hf data, mainly on the *g* value and on the *p*:*m* ratio of the splitting constants in aryl substituents.

$^{\bullet}CR^1R^2(CRO)$

1

a; R = Me, R^1 = H, R^2 = CO_2Et
b; R = H, R^1 = CO_2Et, R^2 = Ph
c; R = Me, R^1 = CO_2Et, R^2 = Ph
d; R = Me, R^1 = H, R^2 = COMe[11]
e; R = Ph, R^1 = H, R^2 = Ph[5]
f; R = Ph, R^1 = Ph, R^2 = COPh
g; R = H, R^1 = Ph, R^2 = Ph[12]
h; R = Me, R^1 = Ph, R^2 = Ph[12]
i; R = Ph, R^1 = Ph, R^2 = Ph[12]

$^{\bullet}CR^3(CN)(CRO)$

2

a; R = H, R^3 = 2,4-Me_2Ph
b; R = Me, R^3 = 2,4-Me_2Ph
c; R = Ph, R^3 = 2,4-Me_2Ph
d; R = H, R^3 = Mes
e; R = Me, R^3 = Mes
f; R = Ph, R^3 = Mes
g; R = Naph, R^3 = Mes

For comparison, EPR data of a few radicals previously described are added.[5,11,12]

Results

The hyperfine splittings and *g* values of radicals **1** and **2** are given in Table 1 and Table 2. The assignment of the splitting constants was made by comparison with the radicals $^{\bullet}CH_2CRO$, $^{\bullet}CH_2R^1$, $^{\bullet}CH_2R^2$ and $^{\bullet}CH_2R^3$. The data for these radicals are listed in Table 3.

$^{\bullet}CH(COOEt)(CMeO)$ (**1a**), $^{\bullet}CPh(COOEt)(CHO)$ (**1b**), $^{\bullet}CPh(COOEt)(CMeO)$ (**1c**).—The radicals are generated by reaction of $Bu^tO^{\bullet}$ with the corresponding methane compounds **3a**, **3b**, **3c** during photochemical decomposition of $(Bu^tO)_2$ in the cavity of the EPR spectrometer.

$$\underset{}{Bu^tO^{\bullet}} + \underset{\textbf{3a–c}}{CHR^1R^2(CRO)} \longrightarrow Bu^tOH + \underset{\textbf{1a–c}}{^{\bullet}CR^1R^2(CRO)} \qquad (3)$$

The spectra were only observed during irradiation. Because of the low intensity of the spectra, about 10 scans were added for getting a sufficient signal-to-noise ratio. Observed and calculated EPR spectra of **1b** are given in Fig. 1. All the splittings observed are found in the spectra of the radicals with a single substituent (see Table 3) with the exception of the β proton splitting in **1b** which is less than 0.02 mT. Radical **1a** has also been observed during the reaction of $HO^{\bullet}$ radicals with **3a** in H_2O.[13]

$^{\bullet}CPh(CPhO)_2$ (**1f**).—The radical has been observed during heating of the dimer **4** in diphenyl ether at $T > 130$ °C. An EPR spectrum taken at $T = 150$ °C is given in Fig. 2.

$$\underset{\textbf{4}}{[CPh(CPhO)_2]_2} \longrightarrow \underset{\textbf{1f}}{2\,^{\bullet}CPh(CPhO)_2} \qquad (4)$$

Besides the expected splittings due to the protons of the phenyl rings in the α position, it shows additional splittings (0.015 mT) caused by four protons of the phenyl rings in the β position. Splittings of that type have not previously been observed.[14]

$^{\bullet}C(2,4\text{-}Me_2Ph)(CN)(CHO)$ (**2a**), $^{\bullet}C(2,4\text{-}Me_2Ph)(CN)(CMeO)$ (**2b**), $^{\bullet}C(2,4\text{-}Me_2Ph)(CN)(CPhO)$ (**2c**).—The radicals have

Table 1 EPR parameters of radicals $^{\bullet}CR^1R^2(CRO)$

Radical	a(H)/mT	g	Solvent	T/K	Δg	$\lvert\rho_p/\rho_m\rvert$
1a	α(1H): 1.89, γ(3H): 0.05, δ(2H): 0.11	2.0051	$(Bu^tO)_2$	265	0.0000	
1a[13]	α: 1.896, δ: 0.113	2.0046	H_2O		0.0002	
1b	δ(2H): 0.055, *o*(2H): 0.385, *m*(2H): 0.140, *p*(1H): 0.469	2.0043	$(Bu^tO)_2$	319	0.0010	3.35
1c	γ(3H): 0.04, δ(2H): 0.08, *o*(2H): 0.455, *m*(2H): 0.150, *p*(1H): 0.525	2.0025	$(Bu^tO)_2$	343	0.0026	3.50
1d[11]	α(1H): 1.79, γ(6H): 0.03	2.0052			0.0004	
1e[5]	α(1 H): 1.404, *o*(2H): 0.41, *m*(2H): 0.14, *p*(1H): 0.494	2.0038			0.0005	3.53
1f	*o*(2H): 0.397, *m*(2H): 0.138, *p*(1H): 0.471, 4H: 0.015	2.0035	Ph_2O	423	0.0025	3.41
1g[12]	β(1H): 0.098, *o*(4H): 0.250, *m*(4H): 0.110, *p*(2H): 0.275	2.0040			0.0006	2.50
1h[12]	γ(3): 0.07, *o*(4H): 0.250, *m*(4H): 0.110, *p*(2H): 0.269	2.0037			0.0007	2.45
1i[12]	*o*(4H): 0.282, *m*(4H): 0.120, *p*(2H): 0.309	2.0033			0.0010	2.58

Table 2 EPR and ENDOR parameters of radicals $^{\bullet}CR^3(CN)(CRO)$

Radical	a(H)/mT, a(N)/mT	g	Solvent	T/K	Δg	$\lvert\rho_p/\rho_m\rvert$
2a	*a*	2.0029	Ph_2O	413	0.0021	
2b	*a*	2.0029	Ph_2O	413	0.0019	
2c	*a*	2.0030	Ph_2O	413	0.0017	
2d	*o*(6H): 0.166, *m*(2H): 0.147, *p*(6H): 0.257, 1N: 0.221	2.0033	Ph_2O	413	0.0017	1.51
2e[b]	*o*(6H): 0.147, *m*(2H): 0.106, *p*(6H): 0.198, 1N: 0.198	2.0033	Toluene	383	0.0015	1.61
2f[c]	*o*(6H): 0.140, *m*(2H): 0.140, *p*(3H): 0.245, 1N: 0.245, 2H: 0.03	2.0037	Toluene	363	0.0010	1.51
2g[d]	*o*(6H): 0.137, *m*(2H): 0.137, *p*(3H): 0.247, 1N: 0.227, 1H: 0.027	2.0036	Toluene	353		1.55

[a] Not resolved. [b] H-ENDOR: 0.11, 0.15, 0.20 mT. [c] H-ENDOR: 0.15, 0.26 mT. [d] H-ENDOR: 0.027, 0.137, 0.247 mT at 350 K.

Table 3 EPR parameters of radicals $^{\bullet}CH_2R'$[14]

R′	g	$a(H_\alpha)$/mT	$a(H_{R'},N_{R'})$/mT	$\Delta g(R')$	$\lvert\rho_p/\rho_m\rvert$	Ref.
H[a]	2.0026	2.28		—		5
CHO[b]	2.0046	1.90	β: 0.05	0.0020		2
CMeO[b]	2.0041	1.97	γ: 0.10	0.0015		3
CMeO[c]	2.0044	1.975	γ: 0.027	0.0018		4
CPhO	2.0043	1.970/1.926		0.0017		5
CO_2Et[b]	2.0033	2.140	δ: 0.165	0.0007		16
Ph	2.0026	1.628	*o*: 0.515, *m*: 0.179, *p*: 0.617	0.0000	3.45	5
p-Tol	2.0026	1.607	*o*: 0.513, *m*: 0.175, *p*(Me): 0.670	0.0000	3.30	17
o-Tol	2.0026	1.593/1.566	*o*: 0.522, *p*: 0.627, *o*(Me): 0.398, *m*: 0.173/0.182	0.0000	3.54	7
CN	2.0030	2.100	N: 0.350	0.0004		8

[a] In H_2O–acetone = 1 ··· 2.5. [b] In H_2O. [c] In acetone.

been observed during heating of the dimers **5a–c** in diphenyl ether at $T > 90$ °C (**2a**), $T > 80$ °C (**2b**), and $T > 60$ °C (**2c**).

$$\underset{\textbf{5a–g}}{[CR^3(CN)(CRO)]_2} \longrightarrow \underset{\textbf{2a–g}}{2\ ^{\bullet}CR^3(CN)(CRO)} \qquad (5)$$

At these temperatures, the concentrations were too low to obtain resolved EPR spectra. At $T = 140$ °C, we got a spectrum from **2c**, but not from **2a** or **2b** because the radicals decomposed too rapidly.

$^{\bullet}CMes(CN)(CHO)$ (**2d**), $^{\bullet}CMes(CN)(CMeO)$ (**2e**), $^{\bullet}CMes(CN)(CPhO)$ (**2f**), $^{\bullet}CMes(CN)(C\text{-}\alpha\text{-}Naph\,O)$ (**2g**).—Solutions of the dimers **5d–g** showed EPR signals at $T > +50$ °C (**2d**), $T < +20$ °C (**2e**), $T < -30$ °C (**2f**), and $T < 40$ °C (**2g**). Well resolved spectra were taken at higher temperatures. A spectrum of **2g** is shown in Fig. **3a**, and a calculated one in Fig. **3b**. In comparison with **1b**, it is striking that no β proton splitting is observed in **2d** and that considerable deviations of the ring proton splittings occur. The mesityl splittings of **2d–g** are similar. No γ methyl proton splittings are observed in **2e**, in contrast to **1c** and **1h**. **2f** shows small splittings of two phenyl protons which are better resolved if a smaller modulation amplitude is used, as is also the case with **1f**. **2g** shows a splitting due to a single proton of the α-naphthyl group.

As the analysis of complex EPR spectra is somewhat arbitrary, we tried to get ENDOR spectra from **2d–g**. We obtained relatively broad, weak signals from **2e** and **2f** and failed to get one with **2d**. The results are similar to the EPR values and support the analysis given above. With **2g**, we got a well resolved ENDOR spectrum which is shown in Fig. 3(*c*). The ESR spectrum in Fig. 3(*b*) has been calculated with the proton splittings obtained from the ENDOR spectrum and the nitrogen splitting given in Table 2.

Discussion

g Values.—By comparing the *g* values given in Tables 1–3, it is obvious that the addition of a second or third substituent to radicals $^{\bullet}CH_2CRO$ changes the *g* values to some degree. It is known that the *g* values of substituted methyl radicals, $g(^{\bullet}CH_2R')$, are higher than the *g* value of the methyl radical, $g(^{\bullet}CH_3)$, if there is some interaction of the unpaired electron with heavy elements like nitrogen or oxygen.[14–20] The difference $\Delta g(R')$ [eqn. (6)] is given in the fifth column of Table 3. It might

$$\Delta g(R') = g(^{\bullet}CH_2R') - g(^{\bullet}CH_3) \qquad (6)$$

be expected that the *g* value of radicals with two or three substituents R′, g_{calc}, would exceed $g(^{\bullet}CH_3)$ by the sum of the

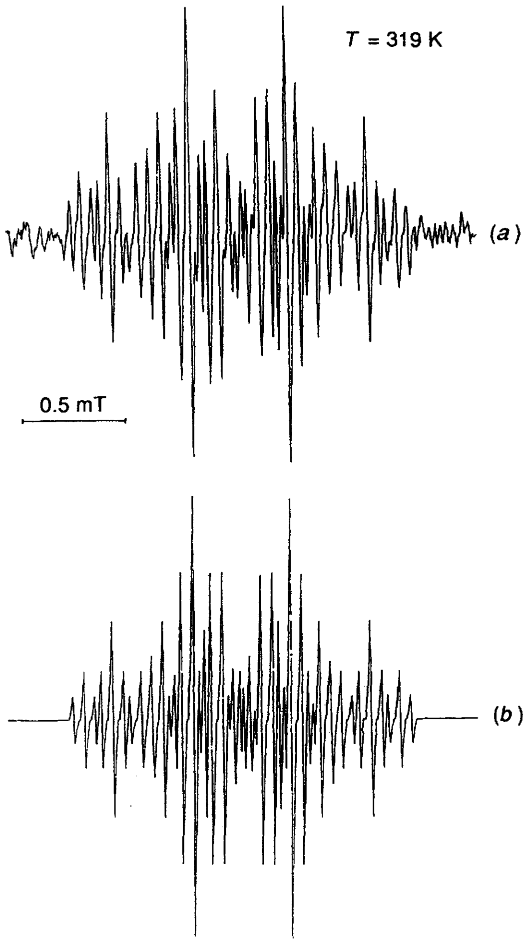


Fig. 1 EPR spectrum of $^{\bullet}CPh(CO_2Et)(CHO)$ (**1b**) (*a*) observed in $(Bu^tO)_2$ at 46 °C and (*b*) calculated with the data given in Table 1

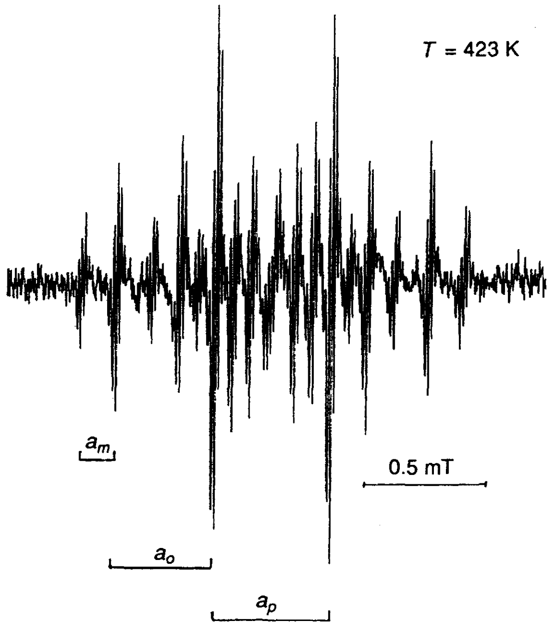


Fig. 2 EPR spectrum of $^{\bullet}CPh(CPhO)_2$ (**1f**) in Ph_2O at 150 °C

deviations for the substituted radicals with a single substituent if there were no interaction between the α substituents.

$$g_{calc} = g(^{\bullet}CH_3) + \sum_{R'} \Delta g(R') \qquad (7)$$

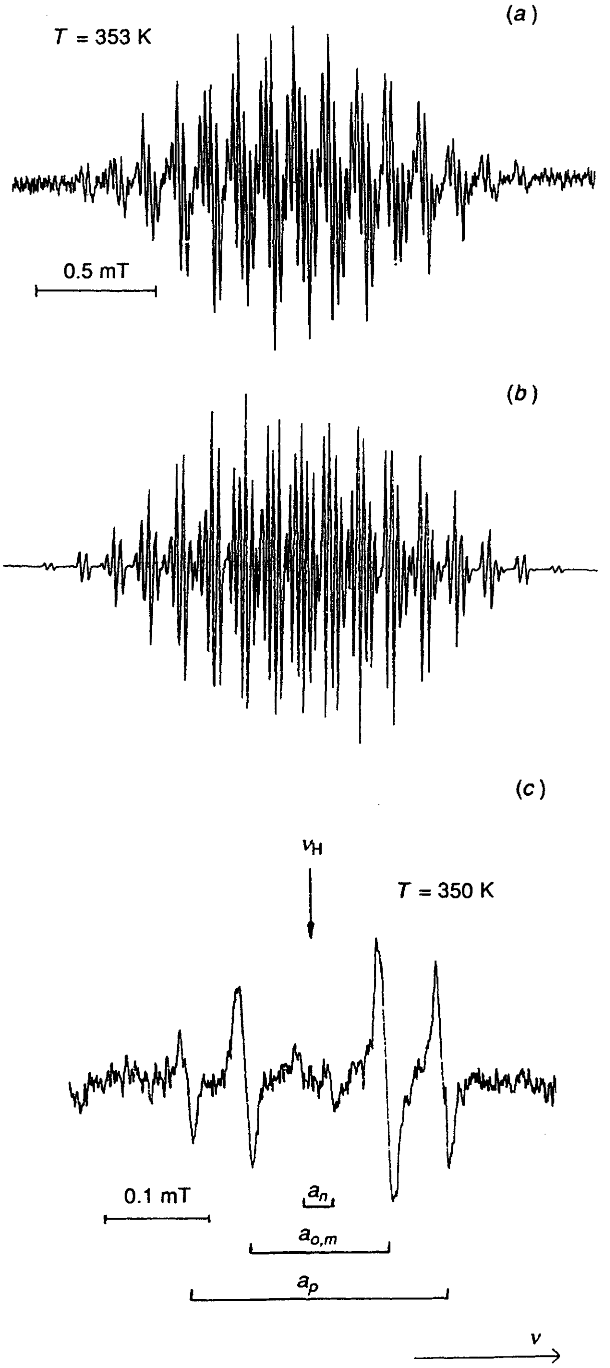


Fig. 3 EPR spectrum of $^{\bullet}CMes(CN)(C\text{–}\alpha\text{-}NaphO)$ (**2g**) observed in toluene at 80 °C. (*b*) EPR spectrum calculated with the data given in Table 2. (*c*) H-ENDOR spectrum in toluene at 77 °C.

Δg Values, the differences between g_{calc} and the experimental g values, g_{exp}, [eqn. (8)] are listed in the sixth column of Tables 1 and 2.

$$\Delta g = g_{calc} - g_{exp} \qquad (8)$$

When applying the eqns. (6)–(8), the solvent dependence of the g values has to be considered. Whereas $g(^{\bullet}CH_3)$ is independent of the solvent, $g(^{\bullet}CH_2CMeO)$ is lower in H_2O (2.0041[3]) than in acetone (2.0044[4]) and in other aprotic solvents. $g(^{\bullet}CH_2CHO)$ and $g(^{\bullet}CH_2CO_2Et)$ are known in H_2O and the g values of all the other radicals have been measured in aprotic solvents. The values in aprotic media were taken if possible, and it is assumed that the H_2O values which had to be taken in the other cases do not differ by too much.

Δg Values are found to be in the range 0.0000–0.0005 in radicals with two substituents, which show no or only small steric hindrance, and between 0.0006 and 0.0026 in radicals with three substituents. This is explained by a twist of the CRO group out of the radical plane because of steric hindrance, which disturbs the delocalisation of the unpaired electron as given in eqn. (1), and thus diminishes the g value. The Δg value might therefore be treated as an indicator for the steric hindrance of the substituents.

Ring Proton Splittings.—Whereas the *m* proton splittings are almost all the same in radicals **1** and **2** with R^1, R^2 or R^3 = Ph ($0.1\ \text{mT} \leqslant a_m \leqslant 0.15\ \text{mT}$), the *o* and *p* proton splittings vary considerably. Such examples have been observed in a few cases[14] and explained by a rotation of the aryl rings which diminishes the delocalisation of the unpaired electron into the aromatic rings and, as a consequence, reduces the splitting constants, particularly in *o* and *p* positions [see eqn. (2)]. We will treat the ratio $|\rho_p/\rho_m|$ as a measure of the distortion of the aryl rings. ρ_p and ρ_m are determined from $a_\alpha = |Q_\alpha|\cdot\rho$ and $a_\beta = Q_\beta\cdot\rho$ with $|Q_\alpha| = 2.5$ mT and $Q_\beta = 2.9$ mT.[20] The results are given in the Tables. The values vary between 3.30 and 3.54 for the planar benzyl, *o*-xylyl, and *p*-xylyl radicals. The radicals **1b–f** with a single phenyl substituent exhibit values between 3.35 and 3.52, the radicals **1g–i** with two phenyl substituents between 2.45 and 2.58, and **2d–g** between 1.51 and 1.66. The substitution of two methyl groups at the *o* positions of the phenyl groups distorts the phenyl rings as does the introduction of a second phenyl group at the radical centre whereas the nature of the other substituents at the radical centre does not affect $|\rho_p/\rho_m|$. This is in contrast to the behaviour of Δg which changes with the nature of the other substituents. The twist of the α-carbonyl groups depends much more on the substituents than that of the aryl groups. This might be explained by the different heights of the rotation barriers (9 kcal mol^{-1} in the acetonyl radical,[6] 13 kcal mol^{-1} in the benzyl radical[7]).*

Proton Splittings in the CRO *and in the* CO_2Et *Group.*—Proton splittings in the formyl and the acetyl groups of **1a–d**, **g**, **h** and **2d**, **e** are smaller than in $^{\bullet}CH_2CHO$ and $^{\bullet}CH_2CMeO$, or absent. In contrast to this, splittings of two phenyl protons are observed in the benzoyl groups of **1f** and **2f**, but not in **1e** and **1i**. Similarly, a single α-naphthyl proton causes splittings in the EPR spectrum of **2g**. Phenyl proton splittings are also observed in *p*-substituted benzoylmethyl radicals.[21] It has been concluded from INDO and CNDO calculations that the biggest splittings are caused by the *o*-protons and that they are sensitive to conformational changes. In contrast to this, splittings observed in benzoyl radicals are caused by the *m*-protons.[22,23] Similarly, the biggest splitting in naphthoyl radicals is caused by the proton in the 3-position.[24] The definitive assignment of the observed splittings in **1f**, **2f** and **2g** should be determined by the investigation of *o*- or *m*-substituted radicals.

Couplings observed in the CO_2Et groups are caused by long-range interactions[13] which are observed in radicals with definite conformations (W or zig-zag arrangement).[25]

Experimental

All reactions with air-sensitive compounds were carried out under dry argon. Instrumentation and the preparation of radical solutions have been described.[26,27]

EPR and ENDOR Spectroscopy.—EPR spectra were recorded using a VARIAN E 109 E instrument equipped with a VARIAN E-900-3 data acquisition system which was also used for the EPR spectra simulations. The g values were determined by use of DPPH† as a reference (g = 2.0036) with an accuracy of *ca.* 0.0001. The microwave frequency was determined using a frequency counter (Hewlett–Packard, 5246 L) with a frequency converter 5255 A. Photochemical experiments were performed with the unfiltered light of a 1000 W high pressure Hg–Xe lamp (HANOVIA 977–B1) focused on the cavity. ENDOR spectra were recorded using an ER 200 D instrument with resonator EN 801.

Radical Precursors (**3–5**).—Ethyl acetoacetate (**3a**) is commercially available (MERCK, Darmstadt). Ethyl α-phenylformylacetate (**3b**) and ethyl α-phenylacetoacetate (**3c**) were synthesised as described elsewhere.[28] HCl was passed into α-phenylformylacetonitrile or α-phenylacetoacetonitrile (0.14 mmol) in EtOH (150 cm^3) at 0 °C until saturation (610 h) and left to stand overnight. After removing the excess HCl with a water-jet pump (0.5 h), the solution was hydrolysed with water (1000 cm^3) and extracted with diethyl ether. The raw product was recrystallised from pentane (*ca.* 50% yield).

1,2,2-Tetrabenzoyl-1,2-diphenylethane was synthesized following the literature.[29] M.p. 203 °C (lit., 203 °C). The precursor compounds **5** of the radicals **2** were synthesised by treating 2,4-dimethylphenylformylacetonitrile (**5a**), mesitylformylacetonitrile (**5d**) or the corresponding acetyl, benzoyl, or α-naphthoyl compound with PbO_2. Details concerning the synthesis and the structure of the dimers **5** will be given elsewhere.[30]

Acknowledgements

Dr. A. Zarkadis thanks the *Deutsche Akademische Austauschdienst* for a Fellowship, Dr. M. Lehnig the *Bruker Analytische Messtechnik GmbH*, Rheinstetten, Germany, for having been able to do the ENDOR measurements in their laboratories, especially Dr. Such for experimental assistance. We are grateful to the *Fonds der Chemischen Industrie* for support.

---

* 1 cal = 4.184 J.

† 2,2-Diphenyl-1-picrylhydrazyl.

References

1 Part 18: W. P. Neumann, A. Penenory, U. Stewen and M. Lehnig, *J. Am. Chem. Soc.*, 1989, **111**, 5845.
2 R. Livingston and H. Zeldes, *J. Am. Chem. Soc.*, 1966, **88**, 107.
3 B. C. Gilbert, J. P. Larkin and R. O. C. Norman, *J. Chem. Soc., Perkin Trans. 2*, 1972, 794.
4 H. Zeldes and R. Livingston, *J. Chem. Phys.*, 1966, **45**, 1946.
5 H. Paul and H. Fischer, *Helv. Chim. Acta*, 1973, **56**, 1575.
6 G. Golde, K. Möbius and W. Kaminski, *Z. Naturforsch., Teil A*, 1969, **24**, 1214.
7 M. S. Conradi, H. Zeldes and R. Livingston, *J. Phys. Chem.*, 1979, **83**, 633, 2160.
8 V. Malatesta, D. Forrest and K. U. Ingold, *J. Phys. Chem.*, 1978, **82**, 2370.
9 J. A. Pople and D. L. Beveridge, *J. Chem. Phys.*, 1968, **49**, 4725.
10 L. Van den Hoek, A. Smidt, W. G. B. Huysmans and W. J. Mijs, *Chem. Phys. Lett.*, 1972, 13.
11 D. J. Edge, B. C. Gilbert, R. O. C. Norman and P. R. West, *J. Chem. Soc. B*, 1971, 189.
12 W. P. Neumann and R. Stapel, *Chem. Ber.*, 1986, **119**, 3422.
13 P. Smith and K. Karukstis, *J. Magn. Reson.*, 1982, **46**, 200; **47**, 8.
14 Landolt-Börnstein, Vol. 9b, 17b, c, *Magnetic Properties of Free Radicals*, ed. Hanns Fischer, Springer-Verlag, Berlin, Heidelberg, New York, 1977, 1987.
15 M. J. Davies, B. C. Gilbert and R. O. C. Norman, *J. Chem. Soc., Perkin Trans. 2*, 1984, 503.
16 G. Behrens, E. Bothe, G. Koltzenburg and D-Schulte-Frohlinde, *J. Chem. Soc., Perkin Trans. 2*, 1981, 143.

17 P. Neta and R. H. Schuler, *J. Phys. Chem.*, 1973, **77**, 1368.

18 R. Livingston and M. Zeldes, *J. Magn. Reson.*, 1969, **1**, 169.

19 H. Itzel and F. Fischer, *Helv. Chim. Acta*, 1976, **59**, 880.

20 K. Scheffler and H. B. Stegmann, *Elektronenspinresonanz*, Springer-Verlag, Berlin, Heidelberg, New York, 1970.

21 J. Bargon, F. Graf, W. Lau and A. C. Ling, *J. Phys. Chem.*, 1979, **83**, 269.

22 P. J. Krusic and T. A. Rettig, *J. Am. Chem. Soc.*, 1970, **92**, 722.

23 L. Grossi and G. Placucci, *J. Chem. Soc., Chem. Commun.*, 1985, 943.

24 D. Casarini, L. Grossi and G. Placucci, *J. Chem. Soc., Perkin Trans. 2*, 1986, 599.

25 F. W. King, *Chem. Rev.*, 1970, **76**, 157.

26 W. P. Neumann, W. Uzick and A. K. Zarkadis, *J. Am. Chem. Soc.*, 1986, **108**, 3762.

27 M. Lehnig and K. Dören, *J. Organomet. Chem.*, 1981, **210**, 331.

28 K. H. Kimball, G. D. Jefferson and A. B. Pike, *Org. Synth.*, Coll. Vol. II, 1966, 284.

29 S. Goldschmidt and F. Nagel, *Ber. Dtsch. Chem. Ges.*, 1930, **63**, 1212.

30 W. P. Neumann, U. Pentling and B. Kubiak, unpublished results.

Paper 2/01826H
Received 30*th March* 1992
Accepted 26*th May* 1992