Electron Spin Resonance Spectra of Some Substituted Methyl Radicals

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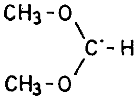
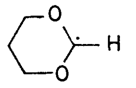
The e.s.r. spectra of methyl radicals bearing alkoxy-, alkylthio-, or chloro-substituents are reported. The coupling constants are discussed in terms of non-planarity of the radical centre.

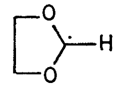
THE geometry at the tervalent carbon atom in organic free radicals is affected by the nature of the substituents attached to this atom and by steric factors such as ring strain. This geometry is reflected by the e.s.r. hyperfine coupling parameters, particularly by those of α-protons, and a combination of the above factors leads to the remarkable variation in the magnitude of this parameter (mT) in the three radicals (I)—(III).[1]



(-)1.19
(I)



(±)0.019
(II)



(+)2.15
(III)

The signs of these coupling constants are unknown; those shown in parentheses were suggested by Dobbs *et al.*[1] and reflect an increasing degree of pyramidality in the series (I)—(III). In a like manner the proton coupling constants of fluoromethyl radicals are thought to pass from the well established −2.2 for $\cdot CH_3$ to +2.22 in $\cdot CHF_2$ as the pyramidality of the carbon centre, reflected by the ^{13}C coupling constant, increases.[2]

We have extended the above studies in two directions. On the one hand we report the results for other cyclic diethers and analogous sulphur–oxygen and sulphur–sulphur systems and on the other we have investigated a number of open-chain chlorine-substituted radicals where the electronegative chlorine substituent might be expected to produce similar effects.[3] We also take this opportunity to report the spectra of a number of other related radicals.

EXPERIMENTAL

All compounds other than those mentioned here were redistilled commercially available products. 1,3-Dithiolan,[4] 1,3-dioxepan,[5] dimethylthiomethane,[4] α-methoxythioanisole,[6] dichloromethyl phenyl ether,[7] and dichloromethyl ethyl ether [8] were prepared by published methods. We thank B.A.S.F. A.G. for a gift of 1,3-dioxocan and Professor E. T. McBee for a gift of *m*-fluoro-ααα-trichloroanisole.

Radicals were generated either by u.v. irradiation at low temperature (typically −50°) in cylindrical thin-walled quartz tubes of a 1 : 1 mixture of di-t-butyl peroxide (Fluka) and the substrate, in which case the radical resulted in the removal of a hydrogen atom by the photochemically generated t-butoxyl radicals (method A), or by reaction of *ca.* 1 : 1 : 1 mixtures of di-t-butyl peroxide, triethylsilane, and the substrate, in which case the radical formed was the result of abstraction of a chlorine atom by the triethylsilyl radical formed by abstraction of a hydrogen atom from triethylsilane (method B). The u.v. source was an Osram 1 000W/4 air-cooled 1 kW high pressure mercury arc focused through a pair of quartz lenses. E.s.r. spectra were measured on a JEOL M.E.IX spectrometer. The magnetic field was calibrated using an n.m.r. marker and a Hewlett–Packard (5 300 A) frequency counter and *g* values were measured with respect to diphenylpicrylhydrazyl (*g* 2.003 6).

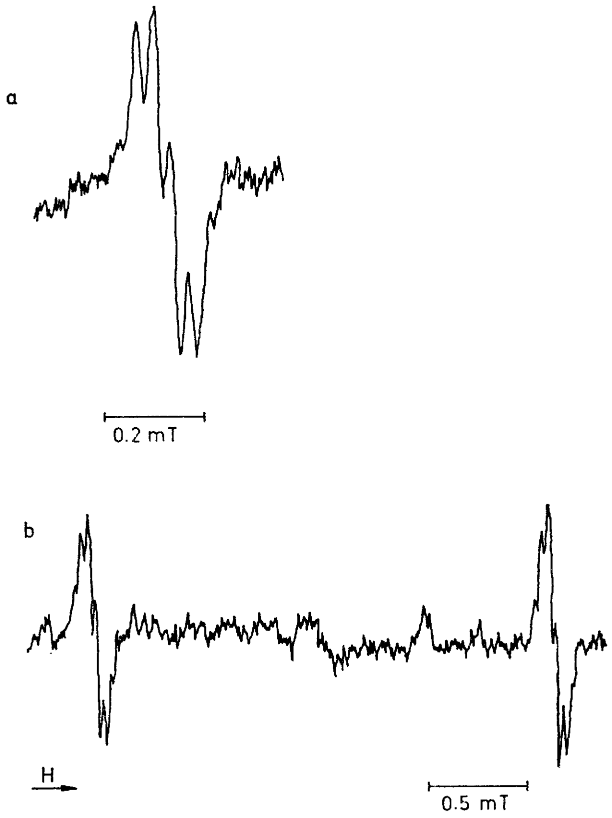


FIGURE 1 E.s.r. spectrum of the radical arising from 1,3-benzodioxole

RESULTS AND DISCUSSION

Table 1 shows the parameters of the radicals arising from the diethers: for (I)—(III) they are essentially the same as those reported in ref. 1 although there are small but significant differences in some cases. This may be due to the fact that in ref. 1 the radicals were

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[1] A. J. Dobbs, B. C. Gilbert, and R. O. C. Norman, *J. Chem. Soc.* (*A*), 1971, 124.

[2] R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, 1965, **43**, 2704.

[3] J. Cooper, A. Hudson, and R. A. Jackson, *Mol. Phys.*, 1972, **23**, 209.

[4] A. Schönberg and K. Praefcke, *Chem. Ber.*, 1967, **100**, 783.

[5] P. A. Laurent, P. Tarte, and B. Rodrigues, *Bull. Soc. chim. France*, 1959, 946.

[6] R. Gerdil, *J. Chem. Soc.* (*B*), 1966, 1071.

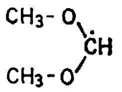
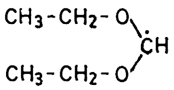
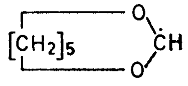
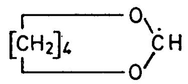
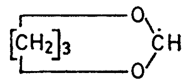
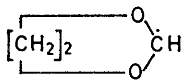
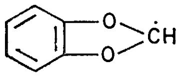
[7] D. H. Holsboer, J. W. Scheeren, and A. P. van der Week, *Rec. Trav. chim.*, 1971, 556.

[8] H. Laato, *Suomen Kem.*, 1959, **32B**, 67.

prepared in aqueous solution using the Ti^{3+}–H^+–H_2O_2 method. The results for the radicals from diethoxymethane, 1,3-dioxepan, 1,3-dioxocan, and 1,3-benzodioxole (IV) confirm the trends reported previously.

TABLE 1

Coupling constants (mT) and *g* values of oxygen-containing methyl radicals

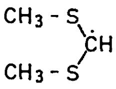
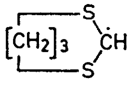
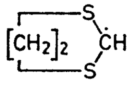
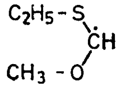
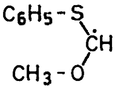
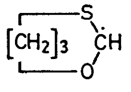
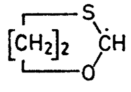
Radical	a_H^α	a_{OH}	*g*
	1.17	0.08 (6)	2.003 0
	1.13	0.08 (4)	2.003 2
	0.00	0.05 (4)	2.003 0
	0.37	0.02 (4)	2.006 0
	0.00	0.02 (4)	2.003 0
	2.17	0.14 (4)	2.003 4
 (IV)	2.36	0.032	2.003 3
$CH_3OCH_2O\dot{C}H_2$	1.76 (2)	0.08 (2)	2.003 3
$C_2H_5OCH_2O\dot{C}HCH_3$	1.43 (1)	0.06 (2), 2.18 (3)	2.003 2

The fine structure of each component of (IV), shown in Figure 1b however presents a problem. Such a sextuplet cannot arise from two pairs of equivalent protons so either the structure of the radical has been wrongly assigned or the radical does not have a plane of symmetry perpendicular to the plane of the benzene ring and containing the tervalent carbon atom. The other main feature of the spectrum of (IV), the doublet splitting of 2.36 mT, and the nature of the substrate makes any other formulation difficult to envisage; it is however equally difficult to imagine how the rigid benzene ring could become deformed.

A possible explanation is that the spectrum does arise from two pairs of equivalent protons with hyperfine coupling constants 0.064 and 0.034 mT respectively. This would yield seven lines with intensity ratios 1 : 2 : 3 : 4 : 3 : 2 : 1 and quite a small asymmetry in the line-breadths, a frequent phenomenon in e.s.r. spectra (see for example Figure 1a), would be sufficient to reduce one of the outer components below noise level and increase the intensity of the other to produce a symmetrical sextet. Such an *ad hoc* explanation is however far from satisfactory and the possibility that the radical arising from 1,3-benzodioxole is not in fact (IV) must be seriously envisaged.

TABLE 2

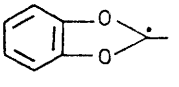
Coupling constants (mT) of sulphur and mixed oxygen–sulphur radicals

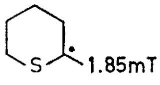
Radical	a_H^α	a_{HO}	*g*
	1.48	0.18 (6) [a]	2.005 1
	1.52	0.15 (4)	2.005 4
	1.35	0.13 (4)	2.005 0
	1.54	0.16 (5)	2.003 0
	1.60	0.20 (3)	2.003 4
	1.44	0.10 (4)	2.003 9
	0.51	0.11 (4)	2.004 1
$CH_3\dot{C}HSCH_2OCH_3$ [b]	1.75 (1)	0.08 (2), 2.09 (3)	2.000 4
$C_6H_5SCH_2O\dot{C}H_2$	1.72 (2)	0.12 (2)	2.003 6

[a] Figures in parentheses are the number of equivalent protons giving rise to the fine structure in question. [b] Radicals arising from hydrogen abstraction from the methoxy-group were not observed.

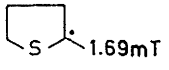
Table 2 shows the results for disulphur and mixed oxygen–sulphur radicals. For the radicals containing only sulphur the coupling constants are all of similar magnitude and there is nothing to suggest that their signs are not all negative and that the tervalent carbon atom is appreciably non-planar. This is in agreement with the fact that the α-coupling in the monosubstituted radicals $RX\dot{C}H_2$ is greater when $X = S$ than when $X = O$ and that the barrier to rotation of the methylene group about the X–C bond is higher in the former than in the latter compound.[9]

The mixed compounds show behaviour intermediate between those of the dioxygen and disulphur compounds. The coupling constants are probably all negative but in the five-membered ring its magnitude is markedly less than in the open-chain or six-membered ring. This may be just due to strain although the coupling constants of the radicals (V) and (VI) are very similar.[9]


(IV)



(V)



(VI)

TABLE 3

Coupling constants (mT) of chloro-substituted methyl radicals

Radical	a_H	a_{Cl}	a_{OR}	g	Substrate	Method of preparation
$CH_3O\dot{C}HCl$	0.31	0.87	0.15	2.004 7	CH_3OCHCl_2	B
$CH_3CH_2O\dot{C}HCl$	0.32	0.86	0.12	2.004 8	$CH_3CH_2OCHCl_2$	B
$ClCH_2O\dot{C}HCl$	0.66	0.66	<0.08	2.005 9	$ClCH_2O{-}CH_2Cl$	A
$C_6H_5O\dot{C}HCl$	0.508	0.676		2.005 1	$C_6H_5OCHCl_2$	B
$CH_3O\dot{C}Cl_2$		1.14	0.10	2.006 3	CH_3OCHCl_2	A *
$CH_3CH_2O\dot{C}Cl_2$		1.13	0.10	2.006 4	$CH_3CH_2OCHCl_2$	A *
$C_6H_5O\dot{C}Cl_2$		1.00		2.006 1	$C_6H_5OCHCl_2$	A
m-$FC_6H_4O\dot{C}Cl_2$		0.96		2.006 3	m-$FC_6H_4OCCl_3$	B

* Radicals arising from hydrogen abstraction from the non-chlorinated alkyl group were not observed.

For the six-membered rings the increase in g factor brought about by passing from an alicyclic (g 2.002 6) to a disubstituted heterocyclic system is 0.000 4, 0.001 3, and 0.002 8 for the O,O, O,S, and S,S systems respectively while in the monosubstituted radicals the excess is 0.000 5 and 0.001 8.[9] The small decrease in g factor brought about by addition of an oxygen atom in going from $RO\dot{C}H_2$ to $(RO)_2CH$ has been attributed to the increased pyramidality of the tervalent carbon atom and to the consequently decreased spin density on the oxygen atoms;[1] the fairly regular increase (0.000 8 and 0.001 0) on adding a further sulphur substituent to either $RO\dot{C}H_2$ or $RS\dot{C}H_2$ shows that the sulphur alone does not appreciably increase the pyramidality of the radical centre. This result supports the suggestion that the low coupling constant in the radical derived from 1,3-oxathiolan stems from a combination of the effects of strain and the electronegativity of the oxygen atom.

Table 3 shows the parameters of several α-chloromethyl radicals together with an indication of the way or ways in which they were produced. The analyses are usually straightforward and in every case confirmed by the spectrum of the corresponding ^{37}Cl species, present in 24.6% abundance, and finally by computer simulation of the sum of these spectra. Figure 2 shows a comparison of experimental and simulated spectra for one of the species discussed here.

Previous work has indicated that the α-proton coupling constants of $CH_3O\dot{C}H_2$ and $(CH_3O)_2\dot{C}H$ given above and of $Cl\dot{C}H_2$ (2.20 mT)[10] and $Cl_2\dot{C}H$ (1.68 mT)[11] are all negative. The signs of the corresponding constants in the alkoxychloromethyl radicals are unknown but whatever they may be it is clear that the passage from either of the two monosubstituted radicals to the mixed species is accompanied by a much larger decrease in the coupling constant than is observed on going to the dichloro or dimethoxyl radicals. The most likely explanation of these low values lies in non-planarity of the radical centre and, as in the case of the cyclic diethers, quite small changes produce very large effects on the coupling constant.

Unless the COC plane is perpendicular to the HCCl plane, the alkoxychloromethyl radicals can in principle exist in the two conformations (VII) and (VIII). We have been unable to find any evidence of the co-existence of these two species inasmuch as the coupling constants are not noticeably temperature-dependent; moreover on steric grounds (VIII) is likely to be more stable than (VII).

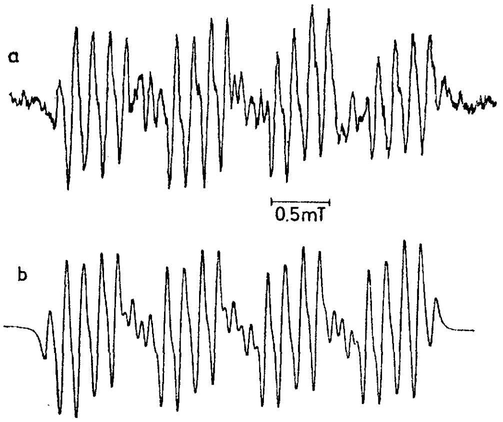


FIGURE 2 a, E.s.r. spectrum of $CH_3O\dot{C}HCl$; b, computer simulation of e.s.r. spectrum of $CH_3O\dot{C}HCl$, including contributions from ^{35}Cl and ^{37}Cl nuclei, using the parameters of Table 2

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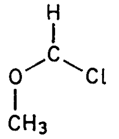
[9] E. A. C. Lucken and B. Poncioni, *Helv. Chim. Acta*, 1972, **55**, 2673.

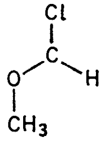
[10] J. P. Michaut and J. Roncin, *Chem. Phys. Letters*, 1971, **12**, 95.

[11] H. Fischer and M. Lehnig, *J. Phys. Chem.*, 1971, **75**, 3410.

Studies of the chlorofluoromethyl radicals $\dot{C}F_nCl_{3-n}$ have shown that the ^{35}Cl coupling constant increases from 0.62 ($n = 0$) through 1.05 ($n = 1$) to 1.61 mT ($n = 2$) as the degree of fluorine substitution increases and this has been interpreted as yet another symptom of non-planarity of the radical centre.[3] The coupling constants of the alkoxy- or aryloxy-dichloromethyl radicals in agreement with the conclusions from the α-proton couplings above, are indeed comparable with that of $\dot{C}FCl_2$. The radical $\dot{C}FHCl$, the analogue of $CH_3O\dot{C}HCl$, does not appear to have been studied but in agreement with the hypothesis of the non-planarity induced by electronegative substituents, the α-^{35}Cl couplings of the monochloroalkoxyl radicals are greater than that (0.28 mT) of $\dot{C}H_2Cl$.



(VII)



(VIII)

If increase in the magnitude of the ^{35}Cl coupling constant is taken as diagnostic of increasing non-planarity and, as seems to be well established, non-planarity makes α-proton coupling constants more positive then, since the lower α-proton coupling in $CH_3O\dot{C}HCl$ compared with that of $ClCH_2O\dot{C}HCl$ is associated with a higher α-^{35}Cl coupling, we may conclude that the α-proton couplings in these radicals have a negative sign.

In these alkoxydichloromethyl radicals there is again the probability that the two chlorine atoms are non-equivalent. The fact that both have the same coupling constant indicates either rapid jumping between the two equivalent conformations with non-identical chlorine atoms or, more unlikely, that the radical does indeed have the symmetrical conformation.

Table 4 shows the parameter for methyl radicals having either an oxygen or sulphur substituent together with a second substituent capable of conjugating with the radical centre. The substituted allyl radicals can exist in *syn-* or *anti*-conformations. The large line-widths (*ca.* 0.2 mT) together with the fact that all three large coupling constants are indistinguishable may indicate that we have in fact a mixture of both forms. The coupling constants for the phenoxyallyl radical are quite similar to those of 1,1-dimethoxyallyl (1.497, 1.443, 0.229 mT)[12] but the phenylthio-substituent has produced a very marked diminution. This reflects the conjugating power of the sulphur atom which was already made manifest by the larger methyl group coupling constant in $CH_3S\dot{C}H_2$ (0.30 mT) than in $CH_3O\dot{C}H_2$ (0.21 mT) and the larger barrier to rotation of the methylene group in the former compound.[9]

TABLE 4

Coupling constants (mT) of miscellaneous radicals. α, β, γ Refer to $CH_3{}^{\beta}CH^{\alpha}OCH_2{}^{\gamma}CO_2H$

Radical	Proton coupling			
	a	β	γ	*g*
$CH_3O{-}\dot{C}H{-}CO_2H$	1.69		0.20	2.003 3
$CH_3O{-}\dot{C}H{-}COCl$	1.57		0.30	2.005 0
$CH_3O{-}\dot{C}H{-}CO_2CH_3$ *	1.76		0.30	2.003 7
$CH_3O{-}\dot{C}H{-}CO_2C_2H_5$ *	1.76		0.30	2.003 7
$CH_3CH_2O{-}\dot{C}HCO_2H$	1.77		0.27	2.004 2
$C_6H_5S{-}\dot{C}H{-}CO_2C_2H_5$	1.50			
$CH_3\dot{C}HOCH_2CO_2H$	1.44	2.20	0.14	2.003 6
$C_6H_5O\dot{C}HCH{=}CH_2$ †	1.40	0.38		2.002 9
$C_6H_5S\dot{C}HCH{=}CH_2$ †	1.13	0.38		2.003 6
$\dot{C}H_2CO_2CH_2CH_3$	2.10			
$OCO_2\dot{C}HCHCl$ ‡	1.59	1.86		2.002 9
$\dot{C}H_2OCH_2Cl$ §	1.86	$1 \leqslant a \leqslant 4$		

* Both these radicals show an additional coupling of *ca.* 0.14 mT arising from the protons of the CO_2CH_2R group. † The protons of the terminal methylene group showed the same coupling as those of the α-protons. ‡ A further splitting from the chlorine-35 atoms of 1.70 mT is present. § Unresolved splitting from the chlorine atom in the range 0.1—0.4 mT is also present.

In all these radicals the magnitude of the α-proton coupling constant shows that the alkoxy-substituent has produced little non-planarity of the radical centre, the ability to conjugate with the second substituent thus appears to be the dominant factor.

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[12] P. J. Krusic, P. Meakin, and B. E. Smart, *J. Amer. Chem. Soc.*, 1974, **96**, 6211.