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AN ELECTRON SPIN RESONANCE STUDY OF THE PHOTOLYSIS OF BIS(β-ALKOXYALKYL)MERCURIALS

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Summary

Bis(β-alkoxyalkyl)mercurials are much more photosensitive than the unsubstituted dialkylmercurials, and when they are irradiated in solution with ultraviolet light, the ESR spectra of the appropriate β-alkoxyalkyl radicals are observed. Spectral data are presented for 14 such radicals and the values of $a(H^{\beta})$ are discussed in terms of possible conformational preferences.

There have been many studies, usually involving ESR spectroscopy, of the homolysis of carbon–metal bonds as the result of bimolecular homolytic substitution (eq. 1) [1], but few instances of photolytic unimolecular carbon–metal homolysis (eq. 2) have been reported.

$$X^{\cdot} + MR \rightarrow X{-}M + R^{\cdot} \qquad (1)$$

$$MR \xrightarrow{h\nu} M^{\cdot} + R^{\cdot} \qquad (2)$$

For example, irradiation of alkyltin(IV) chlorides with ultraviolet light in an ESR cavity shows only very weak spectra of the corresponding alkyl radicals formed by reaction 2, but if di-t-butyl peroxide is added to act as a photolytic source of t-butoxyl radicals, strong spectra are observed of the alkyl radicals resulting from reaction 1 [2]. The only major group of organometallic compounds which is known to undergo reaction 2 is that of the cyclopentadienyl derivatives e.g. $(C_5H_5)_nSnCl_{4-n}$, $(C_5H_5)_2Sn$, $C_5H_5PbPh_3$, $(MeC_5H_4)_2Hg$, Me_5C_5Li, and $(C_5H_5)_2TiCl_2$, and the photolysis of these compounds has provided a useful source of both cyclopentadienyl and metal-centred radicals [3].

The simple organomercury compounds conform to this general pattern, and, for example, ultraviolet irradiation of a solution of dibutylmercury(II) or butylmercury(II) chloride, in an ESR cavity, shows no significant spectrum of the butyl radical [4]. We have found, however, that the introduction of substituents into the alkyl group can greatly increase the photosensitivity, and we report now that

(Continued on p. 4)

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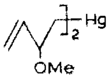
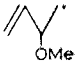
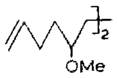
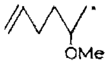
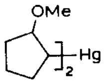
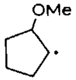
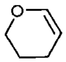
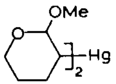
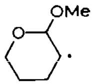
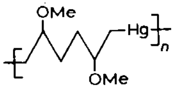
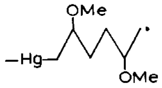
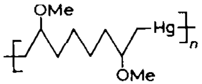
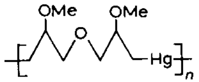
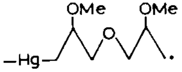
TABLE 1

ESR SPECTRA OF β-ALKOXYALKYL RADICALS

Alkene	Organomercurial	Radical	No.	$a(H^{\alpha})$ (G)	$a(H^{\beta})$ (G)	T (°C)	Solvent
$CH_2{=}CH_2$	$(MeOCH_2CH_2)_2Hg$	$MeOCH_2CH_2^{\cdot}$	1	22.0(2H)	31.3(2H)		Cyclopropane
$BuCH{=}CH_2$	$(MeOCHBuCH_2)_2Hg$[a]	$MeOCHBuCH_2^{\cdot}$	2	22.0(2H)	20.0(2H)	−40	Cyclopropane
$PhMeC{=}CH_2$	$(MeOCMePhCH_2)_2Hg$	$MeOCMePhCH_2^{\cdot}$	3	21.8(2H)	1.5(3H$^{\gamma}$)	0	Cyclopropane
				21.8(2H)	1.5(3H$^{\gamma}$)	−80	
$Ph_2C{=}CH_2$	$(MeOCPh_2CH_2)_2Hg$	$MeOCPh_2CH_2^{\cdot}$	4	21.5(2H)		−20	Cyclopropane
			5	22.0(2H)	24.5(1H)	−130	Cyclopropane
			6	ca.21(2H)	ca.21(1H)	+20	Cyclopropane
$EtOCH{=}CH_2$	$[(EtO)_2CHCH_2]_2Hg$	$(EtO)_2CHCH_2^{\cdot}$	7	22.0(2H)	24.5(1H)	−40	Cyclopropane
				22.0(2H)	25.0(1H)	−110	
$Pr^iOCH{=}CH_2$	$[(Pr^iO)_2CHCH_2]_2Hg$[b]	$(Pr^iO)_2CHCH_2^{\cdot}$	8	22.2(2H)	23.5(1H)	−30	Cyclopropane
				22.2(2H)	25.0(1H)	−110	
$Bu^tOCH{=}CH_2$	$[(Bu^tO)_2CHCH_2]_2Hg$[b]	$(Bu^tO)_2CHCH_2^{\cdot}$	9	22.5(2H)	22.5(1H)	−40	Cyclopropane

			10	22.0(1H$^{\alpha}$)	22.0(1H$^{\beta}$) 36.0(2H)	− 10	Cyclopropane
			11	22(H)	35(2H)	+ 20	Cyclopentane
	 [c]		12	21(2H)	21(1H)	+ 20	Cyclopentane
	 [c]		13	21.5(2H) 22.0(2H)	21.5(1H) 20.25(1H)	+ 10 − 110	Cyclopentane
	 [c]		14	22(2H)	22(1H)	+ 20	Cyclopentane

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[a] The same radical was obtained from the corresponding organomercury(II) chloride in cyclopropane: $a(2H^{\alpha})$ 22.0 G at 0°C and − 100°C, $a(H^{\beta})$ 21.5 G at 0°C and 18.0 G at − 100°C. [b] Prepared from ethyl vinyl ether and $Hg(OAc)_2$ in the appropriate alcohol (ROH). ^{1}H NMR spectra indicated that the products were mixtures of the simple acetals as shown, and of the mixed acetals $[(EtO)(RO)CHCH_2]_2Hg$. All the other mercurials were analytically pure. [c] Prepared from the appropriate diene and $2Hg(OAc)_2$ in MeOH. Mass spectrometry and vapour pressure osmometry showed that $n \approx 5$.

bis(β-alkoxyalkyl)mercurials formed by symmetrization of the products of alkoxymercuration of alkenes (eq. 3), show strong spectra of the corresponding β-alkoxyalkyl radicals on irradiation with ultraviolet light (eq. 4). The one β-alkoxyalkylmercury(II) chloride which we studied behaved similarly.

$$R^1R^2C{=}CHR^3 \xrightarrow[Hg(OAc)_2]{R^4OH} R^1R^2C(OR^4)CHR^3HgOAc \xrightarrow[NaOH]{SnCl_2} [R^1R^2C(OR^4)CHR^3]_2Hg \qquad (3)$$

$$[R^1R^2C(OR^4)CHR^3]_2Hg \overset{h\nu}{\rightarrow} 2R^1R^2C(OR^4)CHR^3 + Hg \qquad (4)$$

The structures of the alkenes, mercurials, and β-alkoxyalkyl radicals, and the ESR parameters of the radicals are shown in Table 1, and a representative spectrum is shown in Fig. 1.

A few β-alkoxyalkyl radicals have been prepared before by various methods, and the ESR spectra have been interpreted in terms of the conformation about the C^{α}–C^{β} bond. The present route to these radicals is the most convenient and versatile, and the spectra of the radicals provide more information about the factors governing their conformations.

The value of $a(H^{\beta})$ in an alkyl radical is usually interpreted in terms of eq. 5, where the term A (ca. 1 G) relates to spin polarisation of the intervening bonding electrons, and the term B (ca. 54 G) arises from hyperconjugative interaction between the singly occupied p-orbital and the C^{β}–H bond, which subtend a dihedral angle of θ [5].

$$a(H^{\beta}) = A + B\cos^2\theta \qquad (5)$$

The β-methoxyethyl radical (Table 1, No. 1) was prepared previously by photolysis of 3-methoxypropionyl peroxide, and the high value of $a(2H^{\beta})$ (31.3 G; cf. $CH_3CH_2^{\cdot}$, $a(3H^{\beta})$ 27.6 G) was ascribed to the fact that the radical is most stable with the methoxyl substituent in the nodal plane of the singly occupied p-orbital, so that the C^{β}–H bonds subtend a small angle (θ) with the axis of the orbital, where

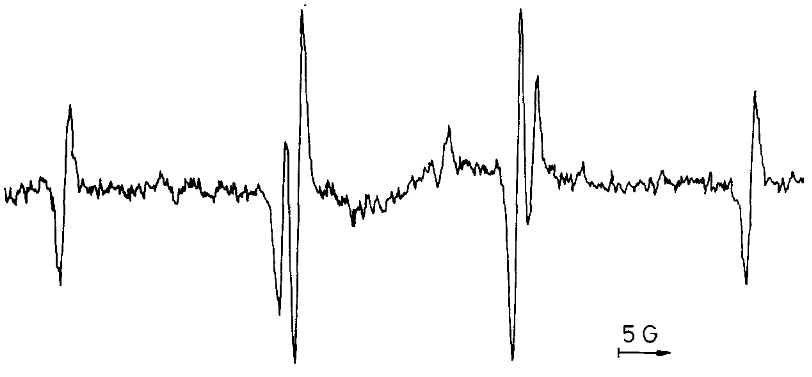
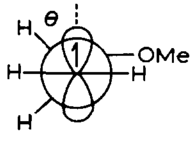
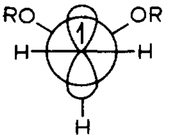


Fig. 1. ESR spectrum of radical 13 obtained from the photolysis of [$CH_2CH(OMe)(CH_2)$ $CH(OMe)CH_2Hg]_n$ in cyclopentane at −67°C.

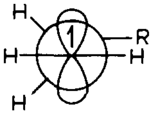
hyperconjugation is efficient (formula I) [6].



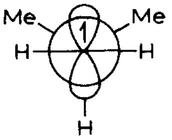
(I)



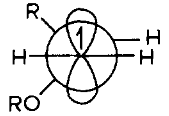
(II)



(III)



(IV)



(V)

The spectrum of the 2,2-diethoxyethyl radical has been observed previously from the reaction of hydroxyl radicals with acetaldehyde diethylacetal in water at neutral pH, and showed $a(H^{\alpha})$ 22.2 G, $a(H^{\beta})$ 27.0 G [7]. The same radical (Table 1, No. 7) in cyclopropane solvent shows a much smaller value of $a(H^{\beta})$ of 24.5 G at $-40°C$ with a small negative temperature coefficient. Our data on the 2,2-diisopropoxy- and 2,2-di-t-butoxy-ethyl radicals (Table 1, No. 8 and 9) are similar. The large difference in $a(H^{\beta})$ in water and in cyclopropane presumably reflects the effect of hydrogen bonding by water to the ethoxy groups. If a single β-methoxy substituent imposes the conformation I, two such substituents might be expected to impose the conformation II, but the low value of the temperature coefficient of $a(H^{\beta})$ suggest that any preference for this conformation is small, and indeed the magnitude of $a(H^{\beta})$ is low even for free rotation about the C^{α}–C^{β} bond. Such low values of $a(H^{\beta})$ are usually ascribed to distortion from tetrahedral structure at C^{β}, the C^{α}–C^{β}–H angle increasing to render interaction of the C^{β}–H σ orbital and the p-orbital less effective.

A single β-alkyl substituent, like a β-alkoxy substituent, tends to lie in the nodal plane of a primary alkyl radical as shown in III, and $a(2H^{\beta})$ decreases as the temperature is raised. No radical appears to have been reported previously where the β-substituents are hydrogen, alkyl, and alkoxy [5]. Our acylic radicals with this composition (Table 1, No. 2, 5, 6, 12, 13 and 14) all show a low value of $a(1H^{\beta})$, and, where it was measured (radicals 2 and 13), the temperature coefficient was small but positive. It thus appears that, despite the propensity of a single β-alkyl or β-alkoxy substituent to lie in the nodal plane (structures III and I, respectively), and of two alkyl substituents (as in $^{\cdot}CH_2CHMe_2$) [5] to impose the eclipsed conformation IV when one of each type of substituent is present, the radical is most stable in the staggered conformation V.

The rings of cyclopentyl radicals are relatively free from conformational complications, and the cyclopentyl radical itself shows values of $a(H^{\alpha})$ 21.48 and $a(4H^{\beta})$ 35.16 G [8]. In the spectrum of the 2-methoxycyclopentyl radical (Table 1, No. 10) which we observed, the two equivalent hyperfine coupling constants of 36.0 G presumably apply to the 5-CH_2 group, and the smaller coupling of 22.0 (1H) refers to the 2-CH group, the spin interaction being reduced by the alkoxy substituent as noted above for the radicals 7, 8, and 9.

The ESR spectrum of the cyclohexyl radical at 10°C appears as a triplet (46 G) of doublets (21 G), but the triplet pattern has been shown to result from hyperfine coupling, not to two equivalent β-protons, but to two non-equivalent pairs; conformational rearrangement results in an alternating line width effect and twelve of the lines are broadened beyond detection [8]. Similarly, at room temperature the tetrahydropyran-3-yl radical shows a doublet (21.2 G) of triplets (46.3 G), rather than a doublet of triplets of triplets [9]. The principal hyperfine coupling constants in the spectrum of our 2-methoxytetrahydropyran-3-yl radical (No. 11) were as noted in Table 1, but the spectrum was too weak to warrant any further interpretation.

The conformations of the radicals (RO)(R′)CHCH$_2^{\cdot}$ (R′ = hydrogen, alkyl or alkoxy) thus appear to be determined by a fine balance of hyperconjugative and steric interactions between the β-substituents and the radical centre, but when the β-alkoxy substituent departs from the nodal plane of the radical, the value of $a(H^{\beta})$ is lower than might be expected.

The enhanced photosensitivity which results from β-alkoxylation may be related to the efficiency with which the light is absorbed, or to weakening of the metal–carbon bond. The relevance of this second factor is emphasised by Barton, Hartwig and Motherwell's recent work on the homolytic reduction of *O*-thiocarbonyl esters and of isonitriles by organotin hydrides [10]. This showed that β-bonded oxygen has a marked effect in stabilising carbon radicals, and that the oxygen can exert this effect even though it lies in the nodal plane of the singly occupied *p*-orbital, so that it cannot become involved in the type of bridging which is recognised for a bromine substituent.

If the photosensitivity which we observe is caused by the stabilisation of the β-alkoxyalkyl radicals, the same effect should be present in similar derivatives of other metals, and it may be possible to exploit this effect in designing, for industrial or agricultural use, organometallic compounds which are photodegradable in the environment.

Experimental

The bis(β-alkoxyalkyl)mercurials were prepared by alkoxymercuration of the appropriate alkenes in alcohol solution with mercury(II) acetate, followed by symmetrization of the resultant organomercury(II) acetates with alkaline tin(II) chloride [11].

The organomercurials were dissolved in cyclopropane or cyclopentane and sealed under vacuum in Suprasil silica tubes. The solutions were irradiated with light from a 500 W high pressure mercury arc in the cavity of a Varian E4 ESR spectrometer.

The products of the photolysis of bis(2-methoxyethyl)mercury were examined by NMR spectroscopy. The neat mercurial was photolysed in a silica tube closed with a rubber serum cap, until 93% of the theoretical yield of mercury had separated (ca. 20 h). The only major organic product was identified as 1,4-dimethoxybutane, $\delta(^1H)$ (C_6H_6) 3.1 (s, 3H, MeO), 3.2 (m, 2H, MeOCH_2), 1.5 ppm (m, 2H, MeOCH$_2$CH_2); $\delta(^{13}C)$ (C_6H_6) 72.65 (MeOCH$_2$), 58.25 (MeO), 26.89 ppm (MeOCH$_2$$CH_2$). For comparison, 1-methoxypropane shows $\delta(^{13}C)$ 75.4 (MeOCH$_2$), 59.1 (MeO), 24.1 ppm (MeOCH$_2$$CH_2$) [12].

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