Phosphoryl- and thiophosphoryl-dithioformates. Part IV. Electrochemical reduction and EPR study of the radical anions†‡

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The reduction of a number of phosphoryl- and thiophosphoryl formates, monothioformates and dithioformates has been studied by means of cyclic voltammetry and EPR spectroscopy. The reduction potentials of all dithioformates are close to −1 V *vs.* SCE, and increase for *S*-alkyl monothioformates and even more for *O*-alkyl monothioformates. The radical anions of the compounds bearing the thiocarbonyl function have been characterised by means of EPR spectroscopy, whereas those of the compounds having the carbonyl function underwent decomposition before detection. Reduction at higher potentials led in most cases to the detection of paramagnetic dianions derived from fragmentation of the initially formed radical anions.

Introduction

In previous studies on phosphoryl- and thiophosphoryl-dithioformates having the general structure $(RO)_2P(X)C(S)SR'$ (with X = O, S) we have shown that these compounds are very efficient spin trapping agents towards a large variety of free radicals in organic media.[1–3] We have also shown that although the spin trapping ability is independent of the nature of the R and R′ substituents, paramagnetic adducts characterised by a greater persistence are formed in the trapping process when phosphoryl dithioformates bearing bulky R groups are used, and, in view of this, methyl bis(2-menthyloxy)phosphoryldithioformate was identified as the best spin trapping agent among the investigated compounds.[3] A water-soluble member of this family has also been synthesised with the aim of using it in biological systems, but when it was exploited as a spin trap in aqueous media it failed to afford detectable radical adducts.[2] The remarkable efficiency of trapping organic radicals of any sort typical of thiocarbonyl compounds,[4–7] combined with the unusually high persistence of the resulting spin adducts, suggested that the title compounds could be used in the polymer industry as inhibitors of auto-oxidative processes. On this basis, some members of the family were tested as stabilisers in the processing of polypropylene and were indeed found to exert a strong protective action against polymer degradation, although there were some drawbacks mainly related to their rather malevolent smell.[3]

Although phosphoryl- and thiophosphoryl-dithioformates proved to be very efficient spin trapping agents, it should be pointed out that the detection of EPR signals in the course of a reaction does not necessarily imply the actual trapping of a free radical (homolytic thiophilic attack of the thiocarbonyl function by a radical $X^{\bullet}$), but may reflect the occurrence of other processes, such as thiophilic attack by a nucleophile followed by oxidation,[8] oxidation of the dithioformate and subsequent attack of the radical cation by a nucleophile (the so called inverted spin trapping[9]), or a single electron transfer (SET) reaction between the phosphoryldithioformate and readily oxidisable compounds present in the system. In particular, it has recently been shown that thiocarbonyl compounds are readily reduced to the corresponding radical anions by Grignard reagents through such SET processes.[2,10]

It is therefore obvious that a knowledge of the reduction potentials of these compounds and of the EPR spectral properties of the corresponding radical anions is a necessary prerequisite to their correct use as spin trapping agents. Although thiocarbonyl compounds are characterised by rather low reduction potentials (certainly lower than those of their oxygen analogues), comparatively few studies have been carried out on their radical anions. EPR spectroscopists first took an interest in thiocarbonyls in the late sixties, when the reduction of thiobenzophenone[11,12] and a number of thiobenzamides[13] was investigated. Studies were carried on in the seventies and early eighties, which may be regarded as the "golden age" of thiocarbonyls from the EPR point of view: again thiobenzophenone derivatives were studied[14] and the radical anion from an aliphatic thioketone, namely hexafluorothioacetone, was first observed.[15] During this period the most conspicuous contribution came from Voss and co-workers, who investigated the radical anions from thio- and dithioesters, thiobenzamides, and di-*tert*-butyl thioketone.[16–18] The studies on aliphatic thioketones published in 1980[19] were followed by a marked decline of interest which has persisted until recent years. All in all, from the available body of information it appears that in aromatic thioketones delocalisation of the unpaired electron onto the aromatic rings is less efficient than in the anion of the corresponding ketones, and that alkyl thioketyls are more similar to alkyl than to thiyl radicals. It is also evident that in all cases the spin density on sulfur is small, and that the radical anions from

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† For Part III, see ref. 3.
‡ Cyclic voltammograms and EPR spectra are available as supplementary data. For direct electronic access see http://www.rsc.org/suppdata/p2/b0/b002986f/

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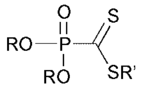
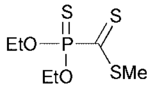
aromatic thiocarbonyl compounds are relatively more persistent than those from aliphatic thiocarbonyls.

We report here the results of a combined electrochemical and EPR investigation into the reduction of phosphoryl- and thiophosphoryldithioformates **1** and **2**, phosphoryl- and thiophosphorylmonothioformates **3**, **4**, **7** and **8**, and of phosphoryl- and thiophosphorylformates **5** and **6**.



1a R = Et, R′ = Me
1b R = Et, R′ = Allyl
1c R = Et, R′ = But-2-enyl
1d R = Et, R′ = But-3-enyl
1e R = Et, R′ = Benzyl
1f R = Et, R′ = Triphenylmethyl
1g R = Et, R′ = Na
1h R = i-Pr, R′ = Me
1i R = 2-Menthyl, R′ = Me
1j R = Lauryl, R′ = Me
1k R = Ph, R′ = Me
1m R = Ph, R′ = Na



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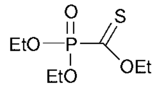

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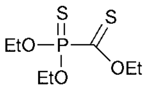

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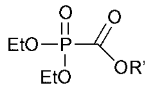
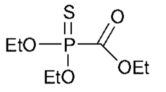


5a R′ = Me
5b R′ = Et
5c R′ = Ph



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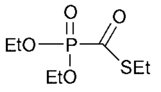

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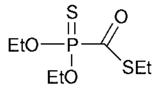

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The reduction of these compounds, which can be considered as aliphatic esters and mono- or dithioesters, is expected to lead to rather unstable radical anions; on the other hand, the presence of the phosphoryl or thiophosphoryl group directly bound to the carbonylic or thiocarbonylic carbon might enhance stability and make possible EPR detection of the radical anions.

Results and discussion

The reduction of compounds **1**–**8** was studied through cyclic voltammetry. Electrochemical reduction was also carried out inside the cavity of an EPR spectrometer and the resulting paramagnetic species were characterised and their spectral parameters determined.

Cyclic voltammetry

The electrochemical reduction of the different compounds has been studied in acetonitrile spanning a potential interval ranging from −0.8 to −2.8 V *vs.* SCE using a glassy carbon electrode. Di- and mono-thioesters of general structure **1**–**4** exhibited a well defined reduction wave (see Table 1) followed by a second irreversible wave at a potential some 800–1000 mV more negative than that of the first reduction. Actually, in some cases the second wave was too close to the background discharge to be properly defined. In most instances the first waves were reversible at relatively low scan rates ($dV/dt \le 0.2$ V s^{-1}, lifetimes of a few seconds), exceptions being provided by compounds **1b**, **1c** and **1e**, whose voltammograms were reversible only at higher scan rates (lifetime around 10^{-2} s). Under the conditions of reversibility of the first wave, the second wave can be ascribed to the further reduction of the radical anion. Different behaviour was exhibited by trityl dithioformate **1f** that also showed two reduction waves; however, the irreversibility of the first wave (even for $dV/dt > 100$ V s^{-1}) did not allow a clear identification of the second. Moreover, the pattern of the voltammogram of **1f** differed from that of the other dithioformates, being characterised by a broad first reduction wave at a more positive reduction potential, thus suggesting a different decay of radical anion **1f**$^{-\bullet}$. Changing the nature of the R and R′ groups in compounds **1a**–**e**, **h**–**k** induced small variations (±100 mV) in the reduction potential, **1f** again being an exception. On the other hand, replacement of the thiocarbonyl group by a carbonyl resulted in significantly more negative reduction potentials (**1a**→**7** −0.68 V, **2**→**8** −0.73 V, **3**→**5b** −1.15 V, and **4**→**6** −1.04 V) and in a dramatic shortening of the lifetime of the reduced species, the voltammograms of compounds **5**–**8** being either irreversible or reversible at scan rates >20 V s^{-1}. Remarkable but less substantial variations of the reduction potentials were also observed when replacing the –SR′ moiety with an –OR′ group (**1a**→**3** −0.4 V, **2**→**4** −0.39 V, **7**→**5b** −0.56 V, and **8**→**6** −0.70 V), the variation being larger for the carbonyl than for the thiocarbonyl derivatives. These trends are consistent with those previously reported for a number of dithio- and monothio-benzoates as well as for some alkoxycarbonyl-substituted dithio- and monothio-formates.[20–23]

Table 1 Reduction potentials (*vs.* SCE) of compounds **1**–**8** and reversibility[a] of the voltammograms

Compound	$E°$/V	Reversibility
$(EtO)_2P(O)C(S)SMe$, **1a**	−1.10	0.1–0.2
$(EtO)_2P(O)C(S)SAllyl$, **1b**	−1.05	5–10
$(EtO)_2P(O)C(S)S$(But-2-enyl), **1c**	−1.05	5–10
$(EtO)_2P(O)C(S)S$(But-3-enyl), **1d**	−1.11	0.1–0.2
$(EtO)_2P(O)C(S)SBenzyl$, **1e**	−1.03	2–5
$(EtO)_2P(O)C(S)SCPh_3$, **1f**	−0.84[b]	>100
$(iPrO)_2P(O)C(S)SMe$, **1h**	−1.13	<0.1
$(2\text{-MenthylO})_2P(O)C(S)SMe$, **1i**	−1.15	<0.1
$(LaurylO)_2P(O)C(S)SMe$, **1j**	−1.10	0.1–0.2
$(PhO)_2P(O)C(S)SMe$, **1k**	−0.94	0.1–0.2
$(EtO)_2P(S)C(S)SMe$, **2**	−1.04	0.1
$(EtO)_2P(O)C(S)OMe$, **3**	−1.47[b]	0.1
$(EtO)_2P(S)C(S)OEt$, **4**	−1.43	0.1
$(EtO)_2P(O)C(O)OMe$, **5a**	Not measured	Not measured
$(EtO)_2P(O)C(O)OEt$, **5b**	−2.64[b]	Irreversible[c]
$(EtO)_2P(O)C(O)OPh$, **5c**	Not measured	Not measured
$(EtO)_2P(S)C(O)OEt$, **6**	−2.47[b]	Irreversible[c]
$(EtO)_2P(O)C(O)SEt$, **7**	−1.88[b]	>100
$(EtO)_2P(S)C(O)SEt$, **8**	−1.77	20–50

[a] Scan rate (V s^{-1}) allowing the observation of the reverse oxidation peak (*ca.* 10%). [b] E_p measured at 0.2 V s^{-1}. [c] The reduction was too close to the background discharge to allow the measurement of reversibility.

Table 2 Reduction potentials[a] of compounds **1a**, **2**, **3**, **4**, and of some reference compounds

Compound	$E°$/V	Reference
$MeC(S)SMe$	∼−1.65	37[b]
$PhC(S)SMe$	−1.32	20, 22
$(EtO)_2P(O)C(S)SMe$, **1a**	−1.10	This work
$(EtO)_2P(S)C(S)SMe$, **2**	−1.04	This work
$MeO(O)CC(S)SMe$	−0.88	20, 22
$MeC(S)OMe$	∼−1.80	37[b]
$PhC(S)OMe$	−1.60	20, 22
$(EtO)_2P(O)C(S)OMe$, **3**	−1.49	This work
$(EtO)_2P(S)C(S)OEt$, **4**	−1.43	This work
$MeO(O)CC(S)OMe$	−1.16	20, 22

[a] In ACN *vs.* SCE. [b] Estimated from the value in 40% propan-2-ol–phosphate buffer.

The values collected in Table 1 also indicate that changing from the phosphoryl to the thiophosphoryl group did not significantly affect either the reduction potentials of the dithioformates or the lifetime of their radical anions; similar substitution in both types of monothioesters, while not leading to large variations in the reduction potentials, resulted in a remarkable enhancement of the stability of the reduced species. The present results indicate that the phosphoryl and thiophosphoryl groups exert a substantially similar electron-withdrawing effect, which, from the data in Table 2, is estimated to be between those of the phenyl and of the methoxycarbonyl groups.

EPR

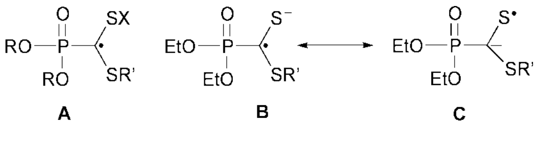
Although the electrochemical reduction of compounds **1**–**8**, carried out in acetonitrile at room temperature inside the cavity

Table 3 Room temperature EPR hyperfine spectral parameters[a] of the radicals observed upon electrochemical reduction of **1**–**8** in ACN

Compound	Radical	$a(^{31}P)$	$a(R')$	$a(^{13}C_\alpha)$	g	Radical	$a(^{31}P)$	$a(^{13}C_\alpha)$	g
1a	$\mathbf{1a}^{-\bullet}$	2.040	0.103 (3H)	2.324	2.0104_5	$\mathbf{9a}^{2-\bullet}$	2.268	2.470	2.0100_0
1b		No signal observed				$\mathbf{9a}^{2-\bullet}$	2.270		2.0100_0
1c		No signal observed				$\mathbf{9a}^{2-\bullet}$	2.269		2.0099_9
1d	$\mathbf{1d}^{-\bullet}$	2.054	n.r.	2.303	2.0104_9				
1e	$\mathbf{1e}^{-\bullet}$	1.980	n.r.	—	2.0105_1	$\mathbf{9a}^{2-\bullet}$	2.250	2.478	2.0100_0
1f		Triphenylmethyl radical observed							
1h	$\mathbf{1h}^{-\bullet}$	2.032	0.110 (3H)	—	2.0103_1				
1i	$\mathbf{1i}^{-\bullet}$	1.980	0.096 (3H)	2.375	2.0103_8	$\mathbf{9i}^{2-\bullet}$	2.159	2.419	2.0100_0
1j	$\mathbf{1j}^{-\bullet}$	2.041	0.098 (3H)	2.339	2.0104_3				
1k	$\mathbf{1k}^{-\bullet}$	1.808	0.086 (3H)	—	2.0112_9	$\mathbf{9k}^{2-\bullet}$	1.933		2.0107_0
2	$\mathbf{2}^{-\bullet}$	1.581	0.123 (3H)	2.292	2.0133_2				
3	$\mathbf{3}^{-\bullet}$	2.341	0.084 (2H)	2.731	2.0070_8				
4	$\mathbf{4}^{-\bullet}$	1.818	0.040 (2H)	2.557	2.0065_7	$\mathbf{12}^{2-\bullet}$	1.705		2.0105_2
5a		Signals (two singlets) not assigned							
5b		Signals (two singlets) not assigned							
5c	$\mathbf{15}^{-\bullet}$	2.456 (2 nuclei with spin $I = \frac{1}{2}$)			2.0056_0				
6	$\mathbf{6}^{-\bullet}$	1.819	0.045 (2H)	2.559	2.0071_7				
7	$\mathbf{15}^{-\bullet}$	2.450 (2 nuclei with spin $I = \frac{1}{2}$)			2.0056_4				
8	$\mathbf{16}^{-\bullet}$	2.140 (2 nuclei with spin $I = \frac{1}{2}$)			2.0041_9	$\mathbf{12}^{2-\bullet}$	1.696		2.0110_5

[a] Coupling constants in mT.

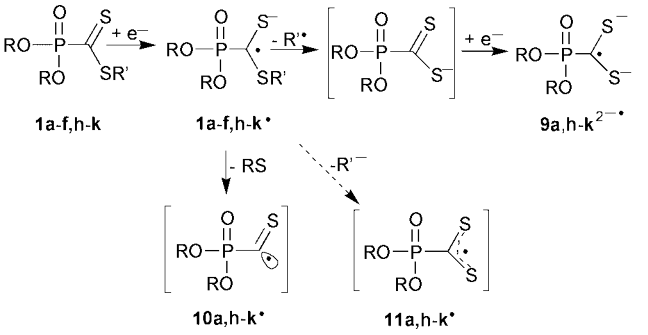
of an EPR spectrometer at potentials close to those reported in Table 1 led in all cases to the detection of EPR spectra, in a few instances the observed signals could not be attributed to the corresponding radical anions. The spectral parameters of all the detected radicals are collected in Table 3. For all the radical anions **1a**–**e**, $\mathbf{h}$–$\mathbf{k}^{-\bullet}$ the spectra consisted of a doublet due to the ^{31}P nucleus, each line of the doublet exhibiting in most cases further hyperfine structure due to hydrogen atoms of the R′ groups. At high amplification satellite lines due to the α-^{13}C nucleus could also be detected. Comparison of the spectral parameters of radical anions **1a**–**e**, $\mathbf{h}$–$\mathbf{k}^{-\bullet}$ with those of the radical adducts $(RO)_2P(O)C(^\bullet)(SX)SR'$ **A** resulting from addition of $X^\bullet$ radicals to the parent compounds[1–3] shows a lower spin density on the central carbon atom in the former species. This is evidenced by the $a(^{13}C_\alpha)$ values which are only *ca.* 63% of that measured for the methyl radical as compared to the ~32 G value found for adducts **A**, *i.e. ca.* 15% less than in the methyl radical. Variations in geometry have recently been shown to be a less important factor than the electronegativity of the substituents in determining hfs constants at a radical centre,[24] and the lower $a(^{13}C_\alpha)$ values exhibited by the radical anions can be more simply attributed to the fact that in these species delocalisation on sulfur is more important than in the adducts **A** (see mesomeric structures **B** and **C**). The delocalisation onto the sulfur atom is also reflected by the higher g-factor values exhibited by **1a**–**e**, $\mathbf{h}$–$\mathbf{k}^{-\bullet}$, *i.e.* $g \geq 2.0100$, compared with those of adducts **A**, *i.e.* $g \approx 2.0065$. As a consequence of the lower spin density on the α-carbon, slightly lower $a(^{31}P)$ couplings are observed for the radical anions than for the adducts.



The series of dithioformates **1a**–**f**, **h**–**k** allows investigation of the effect exerted by different substituents in different positions. Although substitution of the R′ group in the dithioester function does not seem to significantly affect the spin density distribution, it does influence the persistence of the radical anions which in three instances, namely R = allyl, but-2-enyl, and triphenylmethyl, are not detected at all. In particular, when starting from **1f** the well known spectrum of the triphenylmethyl radical is observed, and it would seem that immediately after having been formed, the radical anion undergoes a fragmentation to $Ph_3C^\bullet$ and the diamagnetic dithioformate anion. A similar rapid cleavage of the radical anions $\mathbf{1b}^{-\bullet}$ and $\mathbf{1c}^{-\bullet}$ might explain their elusiveness. In this respect, although one might suggest that the fragmentation of the radical anions **1b**, **c**, $\mathbf{f}^{-\bullet}$ is made easier by the fact that triphenylmethyl as well as allyl and but-2-enyl are stabilised radicals, it is worth noting that the radical anion of the benzylic dithioformate $\mathbf{1e}^{-\bullet}$ was actually observed.

Substitution of the R groups in the alkoxy substituents of the phosphoryl moieties has little effect on the spectral parameters of the radical anions, with the exception of R = phenyl. Actually, radical anion $\mathbf{1k}^{-\bullet}$ exhibited an $a(^{31}P)$ splitting slightly over 18 G, *i.e. ca.* 10% lower than the radical anions from **1a**–**e**, **h**–**j**. The phosphorus atom is directly linked to the radical centre and assuming free rotation about the P–C_α bond, the $a(^{31}P)$ value results from two different contributions: a negative one originating from spin polarisation of the P–C bond, and a positive one due to hyperconjugative interactions between the orbitals of the P=O double bond and the SOMO (singly occupied molecular orbital). Contradictory data concerning the sign of the hfs constant of a phosphorus atom bound to a carbon radical centre can be found in the literature. Thus the phosphorus splitting has been said to be positive in $(C_6H_5)_3P^+CH_2^\bullet$,[25] $Cl_2P(O)CH_2^\bullet$,[26] and $(HO)_2P(O)CH_2^\bullet$,[27] but negative in $(C_6H_5)_2P(O)CH_2^\bullet$.[28] We do not know the sign of the phosphorus splitting in the radicals observed in the present study, and it is not possible to establish which of the two mechanisms causes the lower value of $a(^{31}P)$ exhibited by $\mathbf{1k}^{-\bullet}$.

Prolonged electrolysis resulted in the disappearance of the spectra of the radical anions, which were replaced by simple doublets showing couplings with a single phosphorus atom. Interestingly, the doublet spectrum was also observed in the cases of compounds **1b** and **1c** for which the corresponding radical anions had not been detected. Actually, the same spectrum was observed (see Table 3) with compounds **1a**–**e** bearing the same R substituents (R = ethyl), while somewhat smaller doublets were observed with compounds **1i** (R = 2-menthyl) and **1k** (R = phenyl), bearing different R substituents. As outlined in Scheme 1, three different kinds of radicals might in principle be considered as responsible for these doublet spectra. Thus, loss of an $^\bullet R'$ fragment from the initially formed radical anions would leave the phosphoryldithioformate anions that by further monoelectronic reduction would lead to radical dianions **9a**, **i**, $\mathbf{k}^{2-\bullet}$, for which EPR spectra consistent with the observed doublets are expected.



Scheme 1

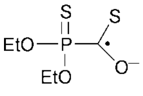
Loss of a R′$^{-}$ carbanion from radical anions **1a**–**e**, **h**–**k**$^{-\bullet}$ would instead lead to radicals **11a**, **h**–**k**$^{\bullet}$, which again might account for the hyperfine parameters of the observed spectra. On the other hand, the loss of such carbanions from the –SR′ group is not an obvious process, most of all when it involves such groups as methyl or but-3-enyl where conjugative stabilisation is not possible. Loss of a thiolate anion, certainly a much easier process, would lead to thioacyls **10a**, **h**–**k**$^{\bullet}$; however, these species cannot be responsible for the detected spectra, because they are σ radicals that should be characterised by $a(^{13}C)$ values larger than 100 G and by *g*-factors much smaller (~2.001) than those actually measured.[29] Indeed the structure of the secondary radicals observed after prolonged electrolysis should not differ significantly from that of the radical anions **1a**–**e**, **h**–**k**$^{-\bullet}$ in view of the similarity of their $a(^{31}P)$, $a(^{13}C)$ splittings and *g*-factors. It should also be stressed that the secondary radicals, likewise **1k**$^{-\bullet}$ as compared to **1a**$^{-\bullet}$, exhibit a noticeable decrease in the phosphorus coupling when replacing the ethyl with a phenyl group in the OR moieties. In view of the above considerations it seems sensible to identify the secondary radicals as the dianions **9**$^{2-\bullet}$, and in order to verify whether these species were indeed responsible for the adventitious spectra, we carried out the electroreduction of sodium diethoxyphosphoryldithioformate **1g** and sodium diphenoxyphosphoryldithioformate **1m** in acetonitrile solutions inside the cavity of the EPR spectrometer. Under conditions similar to those used for the reduction of dithioformates **1a**–**e**, **i**, **k** the EPR spectra observed exhibited in each case an intense doublet which had the same spectral parameters as the secondary radicals already detected in the reduction of **1a**–**e**, **k**, namely $a(^{31}P) = 22.7$ G, $g = 2.0100_1$ and $a(^{31}P) = 19.4$ G, $g = 2.0105_1$, respectively. We can therefore be confident that the identification of the secondary radicals as radical dianions **9a**, **i**, **k**$^{2-\bullet}$ is correct.

As far as the persistence of the radical anions **1a**–**e**, **h**–**k**$^{-\bullet}$ is concerned, the strongest effect is exerted by the 2-menthyl groups, as previously found for the radical adducts of similarly substituted dithioformates,[3] the stabilising action being possibly due to the steric hindrance exerted by the menthyloxy groups.

The radical anion from compound **2**, where a sulfur atom has been substituted for the oxygen atom of the phosphoryl moiety, exhibits a decrease in the phosphorus splitting, negligible variations in the α-^{13}C and the R′ (methyl) splitting, and an increase of the *g*-factor. These data suggest a greater delocalisation on the sulfur of the thiophosphoryl than on the oxygen of the phosphoryl group. The radical anion **3**$^{-\bullet}$ showed the largest ^{31}P and α-^{13}C splittings within the investigated series along with a *g*-factor much smaller than those exhibited by the radical anions **1a**–**e**, **h**–**k**$^{-\bullet}$, thus indicating that in this radical the OR′ moiety is less efficient than the SR′ moiety in delocalising the unpaired electron. Analogously to what was observed when going from **1a**$^{-\bullet}$ to **2**$^{-\bullet}$, switching from **3**$^{-\bullet}$ to **4**$^{-\bullet}$ resulted in a significant decrease in the phosphorus splitting and in relatively small variations of the other spectral parameters. Also, in the case of **4** prolonged electrolysis resulted in the spectrum of the radical anion being replaced by a new signal consisting of a simple doublet (*ca.* 17 G) with a *g*-factor close to 2.01 and by analogy with the reduction of compounds **1**, we tentatively identify this species as the radical dianion **12**$^{2-\bullet}$ that would be formed as outlined in Scheme 1 for radicals **9**$^{2-\bullet}$.

The decay of the EPR signal upon interrupting electrolysis was monitored at room temperature for the radical anions **1a**$^{-\bullet}$ [$k = (3.4 \pm 0.1) \times 10^{-1}$ s^{-1}], **2**$^{-\bullet}$ [$k = (1.9 \pm 0.1) \times 10^{-1}$ s^{-1})], **3**$^{-\bullet}$ [$k = (7.9 \pm 0.8) \times 10^{-2}$ s^{-1}] and **4**$^{-\bullet}$ ($k = 5.3 \pm 0.1) \times 10^{-2}$ s^{-1}]. Consistent with the mechanism proposed in Scheme 1, the decay followed first order kinetics in all cases, the rate constants being similar for the phosphoryl and thiophosphoryl derivatives. The lower values of the decay rate constants (*ca.* one order of magnitude) measured for the radical anions from thioformates than for those from dithioesters may reflect the lower strength of the thioethereal as compared to the ethereal bond. The decrease in the EPR signal from **9**$^{2-\bullet}$ was also found to follow first order kinetics, the decay rate being $k = (6.3 \pm 0.1) \times 10^{-2}$ s^{-1}.

At variance with dithioformates and thioformates **1**–**4**, and as might have been foreseen in the light of the electrochemical results reported in the preceding section, the reduction of formates and thioformates **5**–**8** inside the cavity of the EPR spectrometer proved difficult. Actually, only in the case of **6** could a spectrum consistent with the corresponding radical anion be detected, whereas electroreduction of **5a** and **5b** resulted in each case in the observation of two single lines apparently not correlated with each other. Upon reduction of **5c**, **7** and **8** 1 : 2 : 1 triplets were observed due to radicals where two equivalent phosphorus atoms interact with the unpaired electron (Table 3). In addition, prolonged electrolysis of **8** at higher potentials led to the detection of a 1 : 1 doublet with spectral parameters very close to those of the signal observed by prolonged reduction of **4** and we again assign this doublet to radical dianion **12**$^{2-\bullet}$, as loss of $^{\bullet}$R′ from **4**$^{-\bullet}$ and **8**$^{-\bullet}$ (not observed) leads to the same monothioformate anion. The triplet spectra exhibited by **5c**, **7** and **8** require that two molecules of the starting compounds or their fragments combine together to give either a symmetric radical or a symmetric product that undergoes reduction in the reaction medium.



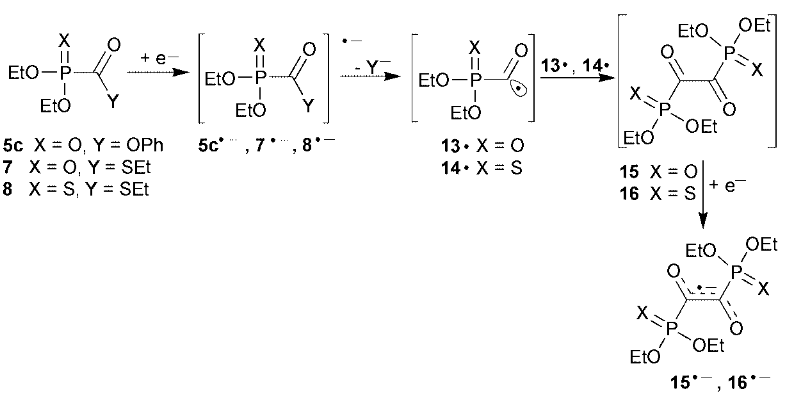
12$^{\bullet 2-}$

Among the possible species that meet these conditions, we favour radical anions **15**$^{-\bullet}$ and **16**$^{-\bullet}$, and outline in Scheme 2 a simple reaction sequence leading to their formation. We have already mentioned the possibility that the radical anions **1**$^{-\bullet}$ undergo the loss of a thiolate anion. In the present case such a process for **7**$^{-\bullet}$ and **8**$^{-\bullet}$, or the loss of a phenolate anion for **5c**$^{-\bullet}$, would produce the acyl radicals **13**$^{\bullet}$ and **14**$^{\bullet}$ whose dimerisation would give the diones **15** and **16** containing two equivalent phosphorus atoms. As soon as they were formed, these diones would undergo reduction to the corresponding radical anions, the species we believe to be responsible for the observed triplet spectra.

Before concluding, it may be worth noting that by combining the electrochemical results (Table 1) with the EPR observations (Table 3) it seems that the limit of voltammetric reversibility allowing the observation of the first electrogenerated radical anions is in the range 1 to 2 V s^{-1}, corresponding to a lifetime of 100 ms or more.

Experimental

The NMR spectra were recorded using a Varian Mercury 400 and a Varian VXR 200 spectrometer.



Scheme 2

Materials

Compounds **1a**, **b**, **d–f**, **i–k**, **2**,[1] **1h**,[30] **3**, **7**,[31] and **5a**,[32] were synthesised according to described procedures. Compound **5b** was a commercial product (Aldrich) as were tetrabutylammonium perchlorate and tetrabutylammonium tetrafluoroborate (Fluka). Acetonitrile (UVASOL, Merck) was purified as previously described.[33] The sodium salts **1g** and **1m** were not isolated but their reduction was carried out on the crude product from the reaction of the sodium salt of the appropriate phosphite with carbon disulfide.[30]

But-2-enyl diethoxyphosphoryldithioformate, 1c. This compound was prepared by reaction of diethyl phosphite with 4-bromobut-2-ene as already described.[34] It was purified by chromatography on silica gel using ethyl acetate–petroleum ether 1:4 as eluant. Deep red liquid, yield 18%. ^{1}H-NMR, 200 MHz, $CDCl_3$—δ in ppm from TMS: 1.36 (t, 6H, J_{HH} = 7 Hz, $\mathbf{CH_3}CH_2O$), 1.67 (d, 3H, J_{HH} = 6 Hz, $CH_2CH{=}CH\mathbf{CH_3}$), 3.83 (d, 2H, J_{HH} = 6 Hz, $\mathbf{CH_2}CH{=}CHCH_3$), 4.22 (dq, 4H, J_{HH} = J_{HP} = 7 Hz, $CH_3\mathbf{CH_2}O$), 5.78 (dt, 1H, $J_{HH_{trans}}$ = 15 Hz, J_{HH} = 6 Hz, $CH_2\mathbf{CH}{=}CHCH_3$), 5.97 (dq, 1H, $J_{HH_{trans}}$ = 15 Hz, J_{HH} = 6 Hz, $CH_2CH{=}\mathbf{CH}CH_3$). ^{13}C-NMR, 50.3 MHz, $CDCl_3$—δ in ppm from TMS: 16.18 (d, J_{CP} = 5.9 Hz, $\mathbf{C}H_3CH_2O$), 17.67 (s, $CH_2CH{=}CH\mathbf{C}H_3$), 37.98 (d, J_{CP} = 2.7 Hz, $\mathbf{C}H_2CH{=}CHCH_3$), 64.50 (d, J_{CP} = 7.0 Hz, $CH_3\mathbf{C}H_2O$), 121.79 (s, $CH_2\mathbf{C}H{=}CHCH_3$), 132.29 (s, $CH_2CH{=}\mathbf{C}HCH_3$), 228.66 (d, J_{CP} = 175.4 Hz, $P\mathbf{C}(S)S$). ^{31}P-NMR, 161.9 MHz, $CDCl_3$—δ in ppm from H_3PO_4 (30% in H_2O): −2.74 (s).

Thiophosphoryl derivatives **4**, **6**, and **8** were all similarly prepared by heating the parent phosphoryl compounds (**3**, **5b**, and **7**, respectively) and an equimolar amount of Lawesson's reagent in toluene at 100 °C for 2 hours in a nitrogen atmosphere. The reaction mixtures were then cooled, filtered, and the solvent was removed in a rotating evaporator. The residues were distilled in a Kugelrohr apparatus under reduced pressure or chromatographed to afford the desired products.

***O*-Ethyl diethoxythiophosphorylthioformate, 4.** Purified by chromatography on silica gel with hexane–ethyl ether 8:2 as eluant. Yellow liquid, yield, 85%. ^{1}H-NMR, 400 MHz, $CDCl_3$—δ in ppm from TMS: 1.39 (td, 6H, J_{HH} = 6.96 Hz, J_{HP} = 0.74 Hz, $\mathbf{CH_3}CH_2O$), 1.49 (td, 3H, J_{HH} = 6.95 Hz, J_{HP} = 1.46 Hz, $OCH_2\mathbf{CH_3}$), 4.31 (dq, 4H, J_{HH} = 6.96 Hz, J_{HP} = 10.24 Hz, $CH_3\mathbf{CH_2}O$), 4.65 (qd, 2H, J_{HH} = 6.95 Hz, J_{HP} = 1.46 Hz, $O\mathbf{CH_2}CH_3$). ^{13}C-NMR, 100.6 MHz, $CDCl_3$—δ in ppm from TMS: 13.55 (s, $OCH_2\mathbf{C}H_3$), 16.31 (d, J_{CP} = 6.94 Hz, $\mathbf{C}H_3CH_2O$), 65.10 (d, J_{CP} = 6.84 Hz, $CH_3\mathbf{C}H_2O$), 69.33 (d, J_{CP} = 6.13 Hz, $O\mathbf{C}H_2CH_3$), 214.77 (d, J_{CP} = 177.86 Hz, $P\mathbf{C}(S)S$). ^{31}P-NMR, 161.9 MHz, $CDCl_3$—δ in ppm from H_3PO_4 (30% in H_2O): 61.39 (s).

Ethyl diethoxythiophosphorylformate, 6. Purified by distillation. Yellow liquid, yield 90%. ^{1}H-NMR, 400 MHz, $CDCl_3$—δ in ppm from TMS: 1.34 (td, 3H, J_{HH} = 6.96 Hz, J_{HP} = 1.83 Hz, $OCH_2\mathbf{CH_3}$), 1.38 (td, 6H, J_{HH} = 6.95 Hz, J_{HP} = 0.73 Hz, $\mathbf{CH_3}CH_2O$), 4.28 (dq, 4H, J_{HH} = 6.95 Hz, J_{HP} = 9.88 Hz, $CH_3\mathbf{CH_2}O$), 4.31 (qd, 2H, J_{HH} = 6.96 Hz, J_{HP} = 1.1 Hz, $O\mathbf{CH_2}CH_3$). ^{13}C-NMR, 50.3 MHz, $CDCl_3$—δ in ppm from TMS: 14.00 (s, $OCH_2\mathbf{C}H_3$), 16.10 (d, J_{CP} = 6.83 Hz, $\mathbf{C}H_3CH_2O$), 62.45 (d, J_{CP} = 4.15 Hz, $O\mathbf{C}H_2CH_3$), 64.61 (d, J_{CP} = 6.59 Hz, $CH_3\mathbf{C}H_2O$), 167.64 (d, J_{CP} = 225.54 Hz, $P\mathbf{C}(O)O$). ^{31}P-NMR, 161.9 MHz, $CDCl_3$—δ in ppm from H_3PO_4 (30% in H_2O): 58.99 (s).

***S*-Ethyl diethoxythiophosphorylthioformate, 8.** Purified by distillation. Colourless liquid, yield 92%. ^{1}H-NMR, 400 MHz, $CDCl_3$—δ in ppm from TMS: 1.30 (td, 3H, J_{HH} 7.6 Hz, J_{HP} = 1.2 Hz, $SCH_2\mathbf{CH_3}$), 1.37 (t, 6H, J_{HH} = 6.8 Hz, $\mathbf{CH_3}CH_2O$), 2.99 (td, 2H, J_{HH} = 7.6 Hz, J_{HP} = 1.6 Hz, $S\mathbf{CH_2}CH_3$), 4.23 (dt, 4H, J_{HH} = 6.8 Hz, J_{HP} = 10.0 Hz, $CH_3\mathbf{CH_2}O$). ^{13}C-NMR, 100.6 MHz, $CDCl_3$—δ in ppm from TMS: 14.16 (s, $SCH_2\mathbf{C}H_3$), 16.26 (d, J_{CP} = 6.8 Hz, $\mathbf{C}H_3CH_2O$), 23.74 (s, $S\mathbf{C}H_2CH_3$), 64.67 (d, J_{CP} = 6.8 Hz, $CH_3\mathbf{C}H_2O$), 198.43 (d, J_{CP} = 161.8 Hz, $P\mathbf{C}(O)S$). ^{31}P-NMR, 161.9 MHz, $CDCl_3$—δ in ppm from H_3PO_4 (30% in H_2O): 61.66 (s).

Phenyl diethoxyphosphorylformate, 5c. Phenyl chloroformate (3.13 g, 0.02 mol) was added dropwise to diethyl phosphite (3.32 g, 0.02 mol) heated at 120 °C under stirring. The mixture was kept at this temperature for 1.5 h after the addition was terminated, then was cooled at room temperature and left standing overnight. The mixture was distilled under reduced pressure (109 °C at 7×10^{-3} mmHg) and **5c** was obtained as a colourless liquid in a quantitative yield. ^{1}H-NMR, 400 MHz, $CDCl_3$—δ in ppm from TMS: 1.45 (td, 6H, J_{HH} = 6.95 Hz, J_{HP} = 0.73 Hz, $\mathbf{CH_3}CH_2O$), 4.40 (dq, 4H, J_{HH} = 6.95 Hz, J_{HP} = 8.06 Hz, $CH_3\mathbf{CH_2}O$), 7.15 (m, $2H_{ortho}$), 7.28 (m, $1H_{para}$), 7.41 (m, $2H_{meta}$). ^{13}C-NMR, 50.3 MHz, $CDCl_3$—δ in ppm from TMS: 15.91 (d, J_{CP} = 11.8 Hz, $\mathbf{C}H_3CH_2O$), 64.56 (d, J_{CP} = 12.9 Hz, $CH_3\mathbf{C}H_2O$), 120.81 (s, C_{ortho}), 126.31 (s, C_{para}), 129.29 (s, C_{meta}), 149.43 (d, J_{CP} = 17.1 Hz, C_{quater}), 165.07 (d, J_{CP} = 545.4 Hz, $P\mathbf{C}(O)O$). ^{31}P-NMR, 161.9 MHz, $CDCl_3$—δ in ppm from H_3PO_4 (30% in H_2O): −7.15 (s).

Electrochemistry

Cyclic voltammetric experiments were performed with a three-electrode set-up using a glassy carbon working electrode (ϕ 0.8–1.0 mm, Tokai Corp.), a platinum counter-electrode, and an aqueous saturated calomel electrode with a salt bridge containing the supporting electrolyte as reference electrode. The working electrode was carefully polished before each set of voltammograms with 1 µm diamond paste and cleansed in an ultrasonic bath with dichloromethane. The electrochemical instrumentation consisted of a PAR Model 175 Universal programmer and of a home-built potentiostat equipped with a positive feedback compensation device.[35] All the cyclic voltammetric experiments were carried out in acetonitrile (ACN) using tetrabutylammonium tetrafluoroborate (0.1 M) as supporting electrolyte in a cell thermostatted at 20 °C. Oxygen was removed from the solutions by bubbling argon. The data were acquired with a 310 Nicolet oscilloscope. The potential values were internally calibrated against the ferrocene/ferricinium couple ($E° = 0.405$ V *vs.* SCE) for each experiment.

EPR spectroscopy

EPR spectra were recorded at room temperature using an upgraded Bruker ER200D/ESP 300 spectrometer equipped with a dedicated data acquisition system, a NMR gaussmeter for the calibration of the magnetic field and a frequency counter for the determination of *g*-factors that were corrected against that of the perylene radical cation in conc. sulfuric acid ($g = 2.00258_3$).[36] The electrochemical cell was home-made and consisted of an EPR flat cell (Wilmad WG-810) equipped with a 25 × 5 × 0.2 mm platinum gauze (cathode), a platinum wire (anode), and a silver wire as reference. The current was supplied and controlled by an AMEL 2051 general-purpose potentiostat. In a typical experiment, the cell was filled with an ACN solution of the appropriate substrate (*ca.* 1×10^{-3} M) containing tetrabutylammonium perchlorate (*ca.* 0.1 M) as supporting electrolyte. After thoroughly purging the solution with argon, spectra were recorded at different potential settings in the range 0 to −5.0 V.

References

1 J. Levillain, S. Masson, A. Hudson and A. Alberti, *J. Am. Chem. Soc.*, 1993, **115**, 8444.

2 A. Alberti, M. Benaglia, M. A. Della Bona, D. Macciantelli, B. Luccioni-Heuzé, S. Masson and A. Hudson, *J. Chem. Soc.*, *Perkin Trans. 2*, 1996, 1057.

3 A. Alberti, M. Benaglia, M. Bonora, V. Borzatta, A. Hudson, D. Macciantelli and S. Masson, *Polym. Degrad. Stab.*, 1998, **62**, 559.

4 J. C. Scaiano and K. U. Ingold, *J. Am. Chem. Soc.*, 1976, **98**, 4727.

5 A. Alberti, B. F. Bonini and G. F. Pedulli, *Tetrahedron Lett.*, 1987, 3737.

6 A. Alberti, M. Benaglia, B. F. Bonini and G. F. Pedulli, *J. Chem. Soc.*, *Faraday Trans. 1*, 1988, **84**, 3347 and references therein.

7 A. Alberti and M. Benaglia, *J. Organomet. Chem.*, 1992, **434**, 151.

8 A. Alberti, P. Carloni, L. Eberson, L. Greci and P. Stipa, *J. Chem. Soc.*, *Perkin Trans. 2*, 1997, 887.

9 L. Eberson, M. P. Hartshorn and O. Persson, *J. Chem. Soc.*, *Perkin Trans. 2*, 1996, 141 and references therein.

10 A. Alberti, M. Benaglia, D. Macciantelli, M. Marcaccio, A. Olmeda, G. F. Pedulli and S. Roffia, *J. Org. Chem.*, 1997, **62**, 6309.

11 E. G. Janzen and C. M. Du Bose, Jr., *J. Phys. Chem.*, 1966, **70**, 3372.

12 H. C. Heller, *J. Am. Chem. Soc.*, 1967, **89**, 4288.

13 J. Voss and W. Walter, *Tetrahedron Lett.*, 1968, 1751.

14 L. Lunazzi, G. Maccagnani, G. Mazzanti and G. Placucci, *J. Chem. Soc. B*, 1971, 162.

15 G. A. Russell, J. L. Gerlock and G. R. Underwood, *J. Am. Chem. Soc.*, 1972, **94**, 5209.

16 J. Voss and K. Schlapkol, *Tetrahedron*, 1975, **31**, 2989.

17 C.-P. Klages and J. Voss, *Angew. Chem.*, *Int. Ed. Engl.*, 1977, **16**, 726.

18 J. Voss and F.-R. Bruhn, *Liebigs Ann. Chem.*, 1979, 1931.

19 C.-P. Klages and J. Voss, *Chem. Ber.*, 1980, **113**, 2255.

20 J. Voss, C. von Bülow, T. Drews and P. Mischke, *Acta Chem. Scand.*, *Ser. B*, 1983, **37**, 519.

21 J. Voss, K. Schlapkohl and W. Schmüser, *J. Chem. Res.* (*S*), 1977, 144; J. Voss, K. Schlapkohl and W. Schmüser, *J. Chem. Res.* (*M*), 1977, 1801.

22 K. Iwai, F. Takemura, M. Furue and S.-I. Nozakura, *Bull. Chem. Soc. Jpn.*, 1984, **57**, 763.

23 H. Viola, H. Hartenhauer and R. Mayer, *Z. Chem.*, 1988, **28**, 269.

24 M. Guerra, *J. Am. Chem. Soc.*, 1993, **115**, 11926; M. Guerra, *J. Phys. Chem.*, 1995, **99**, 81; M. Guerra, *J. Chem. Soc.*, *Perkin Trans. 2*, 1996, 779; M. Guerra, *Res. Chem. Intermed.*, 1996, **22**, 393.

25 J. Weber, L. Ginet and M. Geoffroy, *Chem. Phys. Lett.*, 1976, **41**, 507.

26 S. P. Mishra and M. C. R. Symons, *Faraday Discuss. Chem. Soc.*, 1977, **63**, 175.

27 M. Geoffroy, L. Ginet and E. A. C. Lucken, *Mol. Phys.*, 1979, **37**, 1649.

28 P.-O. Samskog, S. Lee, C. M. Arroyo, L. D. Kispert and M. Geoffroy, *J. Phys. Chem.*, 1984, **88**, 1804.

29 *Landolt-Börnstein*, New Series, Group II, vol. 9 part b, eds. H. Fischer and K. H. Hellwege, Springer-Verlag, Berlin, 1977; *Landolt-Börnstein*, Group II, vol. 17 part b, ed. H. Fischer, Springer-Verlag, Berlin, 1987.

30 D. W. Grisley, *J. Org. Chem.*, 1961, **26**, 2544.

31 L. V. Kovalenko, N. I. Buvashkina and A. V. Sosnov, *Russ. J. Gen. Chem.*, 1994, **64**, 1456.

32 T. Reetz, D. H. Chadwick, E. E. Hardy and S. Kaufman, *J. Am. Chem. Soc.*, 1955, **77**, 3813.

33 F. Paolucci, M. Marcaccio, S. Roffia, G. Orlandi, F. Zerbetto, M. Prato, M. Maggini and G. Scorrano, *J. Am. Chem. Soc.*, 1995, **117**, 6572.

34 A. Bulpin, S. Masson and A. Sene, *Tetrahedron Lett.*, 1989, **30**, 3415.

35 D. Garreau and J.-M. Savéant, *J. Electroanal. Chem.*, 1972, **35**, 309.

36 B. G. Segal, M. Kaplan and G. K. Fraenkel, *J. Chem. Phys.*, 1965, **43**, 4191.

37 R. Mayer, S. Scheihauer and D. Kunz, *Chem. Ber.*, 1966, **99**, 1393.