An Electron Spin Resonance Study of the Reactions of Organosilicon, Organogermanium, and Organotin Radicals with Carbonyl Compounds

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Addition of organosilyl, organogermyl, organotin, and organolead radicals to the oxygen atom of carbonyl compounds has been investigated by e.s.r. spectroscopy. Ease of addition, to a given carbonyl compound, falls in the order $R_3Si\cdot > R_3Ge\cdot \sim R_3Sn\cdot > R_3Pb\cdot$, and for a given Group IVB radical, diketones > oxalates > ketones > trifluoroacetates > formates > acetates. The results are rationalized in terms of bond energy differences, stabilization of radicals formed, and polar effects. Tris(trimethylsilyl)silyl is less reactive than triethylsilyl. Organotin radicals react with α-diketones, oxalates, and quinones to give spectra which are best interpreted as being due to radical anions.

FREE radical additions to carbonyl compounds have received less attention than corresponding additions to alkenes, partly because the stronger π bond in the carbonyl group (312 kJ mol^{-1} in acetone,[1] compared with 249 kJ mol^{-1} in ethylene [2]) makes addition to the carbonyl group less favourable energetically.

However, silanes add across the carbonyl group of ketones in the presence of radical initiators:[3,4] the products formed indicate that a silyl radical adds to the oxygen atom of the carbonyl group[4] [reaction (1; M = Si)] and further evidence for the intermediacy of the adduct radical (I) is provided by its detection by e.s.r. at low temperatures.[5] The occurrence of reaction (1; M = Si) is no doubt facilitated by the strength of the Si–O bond formed during the reaction.

$$XYC{=}O + {\cdot}MR_3 \longrightarrow \underset{(I)}{XY\dot{C}{-}O{-}MR_3} \qquad (1)$$

In this paper, we report an e.s.r. study of the addition of organosilyl, organogermyl, and organotin radicals to a variety of carbonyl compounds, to elucidate the factors which determine whether addition of the radical will or will not take place.

The results for each type of radical are discussed separately, and a comparison is made at the end.

RESULTS AND DISCUSSION

Reactions of Organosilyl Radicals with Carbonyl Compounds.—Trialkylsilyl radicals were prepared by photolysis of t-butyl peroxide and trimethylsilane or triethylsilane in the cavity of a Varian E3 e.s.r. spectrometer.[6] In the presence of a carbonyl compound, the silyl radicals produced by reaction (2) can react by (3) with the carbonyl compound to give the adduct (II).

$$(Bu^tO)_2 \xrightarrow{h\nu} Bu^tO\cdot \xrightarrow{R_3SiH} R_3Si\cdot \qquad (2)$$

$$R_3Si\cdot + O{=}CXY \longrightarrow \underset{(II)}{R_3Si{-}O{-}\dot{C}XY} \qquad (3)$$

If reaction (3) is relatively rapid, the radical (II) only will be observed. If (3) is slow or does not take place, the radical $R_3Si\cdot$ will be seen. In intermediate cases, both $R_3Si\cdot$ and the adduct radical (II) are visible.

The addition of silyl radicals to ketones can also be studied in the absence of di-t-butyl peroxide: here the initiating species is the $^3n,\pi^*$ excited state of the ketone. For example, irradiation of a mixture of acetone and triethylsilane gives superimposed spectra of $CH_3\dot{C}(OH)CH_3$ and $CH_3\dot{C}(OSiEt_3)CH_3$ produced by reactions (4)—(6).

$$CH_3COCH_3 \xrightarrow{h\nu} CH_3COCH_3^* \qquad (4)$$

$$CH_3COCH_3^* + SiEt_3H \longrightarrow CH_3\dot{C}(OH)CH_3 + {\cdot}SiEt_3 \qquad (5)$$

$${\cdot}SiEt_3 + CH_3COCH_3 \longrightarrow CH_3\dot{C}(OSiEt_3)CH_3 \qquad (6)$$

Hydrogen abstraction reactions of photoexcited ketones similar to (5) have been extensively studied by e.s.r. spectroscopy.[7] Similarly photolysis of biacetyl and triethylsilane gives $CH_3\dot{C}(OH)COCH_3$ and an adduct (*cf.* ref. 8). However in the experiments using di-t-butyl peroxide the radicals derived by photoreduction of the ketone are not observed and it would seem that reactions (4) and (5) are insignificant compared with (2) and (3) under our experimental conditions.

The results of our experiments with triethylsilyl radicals are summarized in Tables 1 and 2. The ready addition of silyl radicals to ketones (see ref. 9) is not unexpected: these reactions are very exothermic. Perhaps more surprising is that triethylsilyl radicals do not react with esters such as methyl acetate. In spite of an earlier report [9] that an adduct is formed with methyl acetate we are now unable to detect any addition product from triethylsilyl or trimethylsilyl radicals with methyl acetate over the temperature range used. The species observed in the earlier work was probably the adduct from biacetyl, presumably arising from an impurity in the original methyl acetate. No adduct was observed with methyl propionate or γ-butyrolactone.

Methyl and ethyl formates occupy an intermediate

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[1] R. Walsh and S. W. Benson, *J. Amer. Chem. Soc.*, 1966, **88**, 3480.

[2] S. W. Benson, ' Thermochemical Kinetics,' Wiley, New York, 1968.

[3] R. Calas and N. Duffaut, *Compt. rend.*, 1957, **245**, 906; R. Calas, M.-L. Josien, J. Valade, and M. Villanneau, *ibid.*, 1958, **247**, 2008; A. F. Janzen and C. J. Willis, *Canad. J. Chem.*, 1965, **43**, 3063; E. G. Howard, P. B. Sargeant, and C. G. Krespan, *J. Amer. Chem. Soc.*, 1967, **89**, 1422.

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[5] A. Hudson and R. A. Jackson, *Chem. Comm.*, 1969, 1323.

[6] S. W. Bennett, C. Eaborn, A. Hudson, R. A. Jackson, and K. D. J. Root, *J. Chem. Sic.* (*A*), 1970, 348.

[7] H. Zeldes and R. Livingston, *J. Chem. Phys.*, 1966, **45**, 1946; H. Paul and H. Fischer, *Chem. Comm.*, 1971, 1038.

[8] H. Zeldes and R. Livingston, *J. Chem. Phys.*, 1967, **47**, 1465.

[9] A. J. Bowles, A. Hudson, and R. A. Jackson, *J. Chem. Soc.* (*B*), 1971, 1947.

TABLE 1

Reactions of triethylsilyl radicals with esters and anhydrides

Substrate	Temp (°C)	Radical observed	Comments
HCO_2Me *	−100 to 0	Adduct † + $Et_3Si\cdot$	[Adduct]/[$Et_3Si\cdot$] increases with increasing temperature
HCO_2Et *	−100 to 0	Adduct, $Et_3Si\cdot$	As above
HCO_2Bu^t	−40	Adduct, $Et_3Si\cdot$, $Bu^t\cdot$, $Bu^t O_2C\cdot$, and another doublet	
$MeCO_2Me$ *	−100 to +10	$Et_3Si\cdot$	No addition
$MeCH_2CO_2Me$ *	−60 to +30	$Et_3Si\cdot$, broad lines at higher temperatures	No addition: broad lines at higher temperatures not attributable to adduct
γ-Butyrolactone	−80, 0	$Et_3Si\cdot$	No addition
$CH_2(CO_2Me)_2$ *	−80 to +10	$Et_3Si\cdot$	No addition
$CF_3CO_2CH_3$	−90 to +40	Adduct	
$CF_3CO_2CH_2CH_3$	−90 to +30	Adduct	
$C_2F_5CO_2CH_3$	−80 to +20	Adduct	
$C_3F_7CO_2CH_3$	+10	Adduct	
$(C_3F_7CO)_2O$	−40, 0	Adduct	
$MeOCO_2Me$ *	−20, +10	$Et_3Si\cdot$, broad lines	No addition
$(CH_3CO)_2O$	−80, −40	Adduct	
$(CO_2Et)_2$	−80 to 0	Adduct	
$CH_3CO_2CH_2CF_3$	−40 to +40	$Et_3Si\cdot$	
$CH_3COCH_2CO_2Et$	−40	Ketone adduct	

* Similar results for these substrates were also obtained with trimethylsilyl radicals. † Adduct implies the radical formed by addition of a triethylsilyl radical to the oxygen atom of the carbonyl group.

TABLE 2

Reactions of triethylsilyl radicals with carbonyl and related compounds

Substrate	Temp (°C)	Radical observed	Comments
CH_2O	−100 to −40	Adduct	The same radical has been obtained from CH_3OSiEt_3 + $Bu^tO\cdot$
MeCOCOMe	−40, 0	Adduct	
MeCOCl	−60	Adduct of MeCOCOMe	Identical spectrum to above
PhCOCOPh	−40 to +30	Adduct	Better resolved spectrum at higher temperatures
Me_2NCHO	−105 to −40	$Me_2N{-}\dot{C}{=}O$	Preferential abstraction from DMF rather than Et_3SiH (*cf.* ref. 15)
$MeCOCH_2COMe$	−55	$MeC(OH){=}CH{\cdot}\dot{C}(Me)OSiEt_3$	Adduct of enol form only

position with respect to ketones and acetates: formate adducts and trialkylsilyl radicals are both observed, with the adduct relatively more important at higher temperatures. This implies that there is a significant activation energy for the addition, even though the reaction is exothermic. The decrease in reactivity in the series ketones > formates > acetates presumably reflects activation energy differences. The unreactivity of the esters may reflect their ground state stabilization,† but polar

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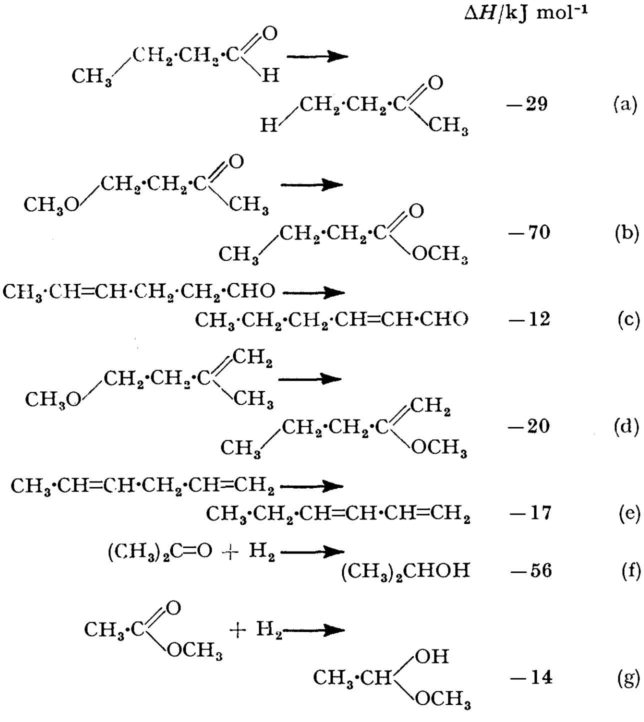
† Data for calculation of π bond energies in esters is not available. Roberts and Caserio[10] estimate the stabilization energy in methyl acetate to be 63 kJ mol^{-1}, based on data from Cottrell's and Pauling's books.[11] Use of Benson's group additivity method[2,12] (which usually gives good agreement with experimental values for unstrained compounds) to calculate heats of formation and hence the heats of the hypothetical reactions (a)—(g) suggest that this estimate is of the right order of magnitude. Thus isomerization (b) gives a decrease in heat of formation of 70 kJ mol^{-1}, much of which can be attributed to the stabilization of the carbonyl group by a lone pair of electrons on the methoxy-oxygen atom. It may be noted in passing that isomerization (a), which does not involve an increase in conjugation, but only formation of a $C_{sp^2}{-}C_{sp^3}$ bond instead of a $C_{sp^3}{-}C_{sp^3}$ bond is also exothermic, but only by 29 kJ mol^{-1} Conjugation of a C=C bond with the carbonyl group (c), a C=C bond with a methoxy-group (d), or two C=C groups with each other (e) appear to be considerably less effective in lowering the energy of the system than conjugation of an alkoxy-group with the carbonyl group (b): it seems reasonable that, in resonance terms, charged contributions from structures of the type $R{-}C({=}\overset{+}{O}R)O^-$ should be more important in esters than are charged structures in the other classes of compound.

Calculated heats of hydrogenation for reactions (f) and (g) also support the idea of a substantial stabilization in the ester group. This stabilization will be lost if the carbonyl π bond is broken by addition of a silyl radical to the oxygen atom, though some of this loss will be offset by the stabilization in the resulting radical by the adjacent alkoxy-group.



[10] J. D. Roberts and M. C. Caserio, 'Basic Principles of Organic Chemistry,' Benjamin, New York, 1965.

[11] T. L. Cottrell, 'The Strengths of Chemical Bonds,' Butterworths, London, 1958; L. Pauling, 'The Nature of the Chemical Bond,' Cornell University Press, Ithaca, 1960.

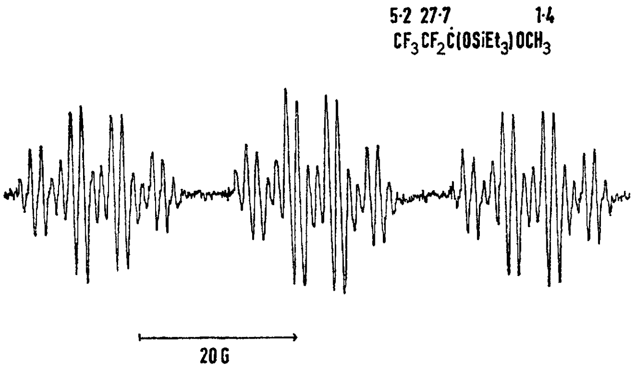
[12] S. W. Benson, F. R. Cruickshank, D. M. Golden, G. R. Haugen, H. E. O'Neal, A. S. Rodgers, R. Shaw, and R. Walsh, *Chem. Rev.*, 1969, **69**, 279.

effects are likely to be important too. Esters are less readily reduced than ketones by electron transfer (*e.g.* by metals) which implies that ketones more readily accept electrons and thus contributions of type (IIIc) to the transition state will be more important.

$$\underset{\text{(IIIa)}}{R_2C{=}O\ \cdot SiEt_3} \longleftrightarrow \underset{\text{(IIIb)}}{R_2\dot{C}{-}O{-}SiEt_3} \longleftrightarrow \underset{\text{(IIIc)}}{R_2\dot{C}{-}O^-\ {}^+SiEt_3}$$

Steric effects are probably relatively unimportant, in view of the unreactivity of γ-butyrolactone.

The significance of polar effects in these reactions is also indicated by the fact that methyl trifluoroacetate and esters of higher fluorinated acids form adducts, as do anhydrides: electron-withdrawing groups will tend to stabilize negative charge on the organic molecule in the transition state. The electron-withdrawing effect of the second carboxy-group in dimethyl malonate is apparently not enough to allow addition to take place.



E.s.r. spectrum of a typical adduct formed from methyl pentafluoropropionate

The non-reactivity of dimethyl carbonate is not surprising. Methyl acetate may be thought of as being formed by substitution of a methoxy-group for a methyl

MeCOMe	$MeCO_2Me$	$MeOCO_2Me$
adduct	no adduct	no adduct

group in acetone, and this process is repeated for dimethyl carbonate.

The e.s.r. spectrum of a typical adduct formed from methyl pentafluoropropionate is shown in the Figure. As the temperature is lowered below 0 °C all of the adducts from esters of perfluoro-acids exhibit alternating line widths in their e.s.r. spectra attributable to restricted rotation of the perfluoroalkyl groups. Similar effects have been noted previously for the radical $CF_3\dot{C}(OSiEt_3)OH$ derived from trifluoroacetic acid.[5]

The non-reactivity of esters towards addition of triethylsilyl radicals was unexpected, in view of the strength of the Si–O bond.[13] However, for esters where the adduct radical is stabilized by conjugation, addition should be facilitated. Thus although methyl acetate does not undergo addition, diethyl oxalate gives the stabilized adduct $EtOCO{\cdot}\dot{C}(OEt)OSiEt_3 \longleftrightarrow EtOC(O{\cdot}){=}C(OEt){-}OSiEt_3$. The e.s.r. spectrum in this case showed some asymmetry, probably due to the superposition of spectra from *cis*- and *trans*-isomers. *cis*- and *trans*-isomers of $EtOCO{\cdot}\dot{C}(OH)OEt$ have been reported by Zeldes and Livingston.[14]

The behaviour of bifunctional compounds confirms the relative unreactivity of the ester grouping: triethylsilyl radicals add to isopropenyl acetate[9] and to ethyl acetoacetate at the carbon–carbon double bond and the carbonyl oxygen atoms respectively. Biacetyl reacts to give a relatively stable adduct: it is possible that this exists in two geometrically isomeric forms (*cf.* ref. 8), but one species (probably the *trans*) predominates. Acetylacetone reacts to give the adduct of the enol form; this adduct is stabilized, whereas that from the corresponding keto-form would not be.

t-Butoxyl radicals appear to react preferentially with dimethylformamide rather than triethylsilane, by abstraction of hydrogen from the CHO group (*cf.* ref. 15); the triethylsilyl adduct radical is not seen. Although methyl and ethyl formates react to give adducts (along with triethylsilyl radicals), t-butyl formate reacts to give a complex spectrum, explicable in terms of $Et_3Si{\cdot}$, the adduct, ${\cdot}CO_2Bu^t$ (presumably formed by hydrogen abstraction), t-butyl (by fragmentation of the previous radical, *cf.* ref. 16), and an unidentified doublet. Acetyl chloride gives the same adduct as biacetyl, presumably by an indirect process involving either halogen abstraction or addition to the carbonyl group by a triethylsilyl radical, followed by further attack on another acetyl chloride molecule.

Triethylgermyl Radical Reactions.—Triethylgermyl radicals were produced analogously to triethylsilyl radicals. Splittings of 4·9 and 0·44 G due to the α- and β-protons were observed.

The Ge–O bond is apparently weaker than the Si–O bond:[13] thus addition of triethylgermyl radicals to carbonyl groups should not be so favourable as triethylsilyl addition. In accordance with this, we find (see Table 3) that although triethylgermyl radicals will add to acetone, the addition is incomplete, and both adduct and triethylgermyl radical spectra are seen. No addition to ethyl trifluoroacetate or to methyl formate occurs,

TABLE 3

Reactions of triethylgermyl radicals with carbonyl compounds

Substrate	Temp. (°C)	Radical	Comments
MeCOCOMe	−20	Adduct	
PhCOCOPh	0 to 40	Adduct?	Spectrum not completely resolved
MeCOMe	0	Adduct + $Et_3Ge{\cdot}$	
$(CO_2Et)_2$	0, +20	Adduct + $Et_3Ge{\cdot}$	
HCO_2Me	0	$Et_3Ge{\cdot}$	
CF_3CO_2Et	−10 to +20	$Et_3Ge{\cdot}$	

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[13] R. A. Jackson, *Chem. Soc. Special Publ.*, No. 24, London, 1970, p. 295.

[14] H. Zeldes and R. Livingston, *J. Phys. Chem.*, 1970, **74**, 3336.

[15] H. Hefter and H. Fischer *Ber. Bunsengesellschaft Phys. Chem.*, 1970, **74**, 493.

[16] D. Griller and B. P. Roberts, *J.C.S. Perkin II*, 1972, 747.

although both these compounds react with triethylsilyl radicals. Diethyl oxalate is apparently about as reactive as acetone towards triethylgermyl radicals, and both the adduct and triethylgermyl radicals are seen. The diketones benzil and biacetyl give adducts: the biacetyl adduct may have a second (geometrical) isomer present in small amounts.

Tri-n-butyltin Radical Reactions.—Photolysis of hexa-n-butylditin with t-butyl peroxide [reaction (7)] was used as a source of tri-n-butyltin radicals.[17] Organotin and organolead radicals suffer from one disadvantage compared with the corresponding silicon and germanium

$$(\mathrm{Bu^tO})_2 \xrightarrow{h\nu} 2\mathrm{Bu^tO}\cdot \xrightarrow{\mathrm{Bu^n_3SnSnBu^n_3}} \mathrm{Bu^tOSnBu^n_3} + \mathrm{SnBu^n_3}\cdot \qquad (7)$$

radicals: because of increased spin–orbit coupling the e.s.r. lines are normally too broad for observation in solution (although $\mathrm{Me_3Sn}\cdot$ has been reported[18]). Consequently only the adduct radicals are easily detectable and conclusions about the relative ease of addition to a range of substrates are more tentative.

The reactivity of tri-n-butyltin radicals with ketones and esters seems to be similar to that of triethylgermyl radicals (Table 4). Thus acetone reacts whereas methyl formate and methyl trifluoroacetate do not.

However the reaction with α-dicarbonyl compounds is more distinctive and of greater interest. With biacetyl, a seven line spectrum is produced indicating equivalence of the two methyl groups. The hyperfine splitting of 7·2 G is close to that found for the biacetyl semidione radical which has been the subject of numerous e.s.r. studies.[19] This suggests that the observed species is best formulated as a radical anion, rather than as a species with predominantly covalent Sn–O bonds. Similarly *para*-benzoquinone gave a five line spectrum ($a_{\mathrm{H}} =$ 2·4 G) attributable to the semiquinone radical anion. The adducts observed with diethyl oxalate and benzil are probably also best thought of as radical anions. This behaviour is to be contrasted with the unsymmetrical adducts formed by silyl or germyl radicals with the same substrates.

TABLE 4

Reactions of tributyltin radicals

Substrate	Temp. (°C)	Radical	Comments
MeCOMe		Adduct	
$\mathrm{HCO_2Me}$	−60 to 0		No addition
$\mathrm{CF_3CO_2Me}$	−40, 0		No addition
MeCOCOMe	−40 to +55	Radical anion	See text
PhCOCOPh	0, +20	Radical anion?	
$\mathrm{(CO_2Et)_2}$	−40 to +20	Radical anion?	
Benzoquinone	0 to 50	Radical anion	

The precise nature of the species observed is open to speculation. A preliminary investigation of the temperature dependence of the e.s.r. spectra has revealed the presence of line-width alternation. This is particularly evident in the case of *para*-benzosemiquinone. At 0 °C the $m_I = \pm 1$ lines of the hyperfine quintet exhibit a marked broadening; the peak amplitudes approach the expected 1 : 4 : 6 : 4 : 1 pattern as the temperature is raised. This type of behaviour is well known in the e.s.r. spectra of semiquinone ion pairs[20] and is generally associated with an oscillation or jump of the counter-ion between two sites which modulates the hyperfine coupling constants. It is possible that the temperature dependent line-width effects we have observed are associated with similar dynamic processes. The apparent equivalence of the four ring protons in the semiquinone could arise from a rapid oscillation of a trialkyltin cation between the two oxygen atoms. Line-width alternation is also apparent in the biacetyl anion. This would seem to rule against a *cis*-semidione with the tin cation symmetrically situated between the two oxygen atoms. The observed spectrum is consistent with a *trans*-semidione and rapid migration of the cation but a *cis*-structure in which the cation is alternately associated with each oxygen cannot be ruled out. We plan to carry out a more detailed investigation of these and related systems with the aim of more precisely defining the structure of the observed radical intermediates. Our present results establish that trialkyltin radicals behave quite differently from silicon and germanium radicals in the presence of α-dicarbonyl compounds.

Lead Radicals.—Trimethyl-lead radicals, prepared by photolysis of hexamethyldilead, do not react with acetone or benzophenone.

Tris(trimethylsilyl)silyl.—In previous studies we have observed that tris(trimethylsilyl)silyl is a somewhat longer lived radical than alkyl-substituted silyl radicals: we have argued that the radical is more planar and there is probably some delocalization of the unpaired electron.[21] Both stabilization effects and steric hindrance should inhibit the addition of this radical to carbonyl compounds, and this is what we observe. In contrast to triethylsilyl, the reaction of tris(trimethylsilyl)silyl with

TABLE 5

Reactions of tris(trimethylsilyl)silyl radicals

Substrate	Temp. (°C)	Radical	Comments
$\mathrm{CF_3CO_2Et}$	0	$\mathrm{(Me_3Si)_3Si}\cdot$	Contrast $\mathrm{Et_3Si}\cdot$
MeCOMe	−40, 10	$\mathrm{(Me_3Si)_3Si}\cdot$	
	+40	$\mathrm{(Me_3Si)_3Si}\cdot$ + adduct	Adduct signal weak even at + 40
$\mathrm{(CO_2Et)_2}$	−40	Mainly $\mathrm{(Me_3Si)_3Si}\cdot$	
	+10	$\mathrm{(Me_3Si)_3Si}\cdot$ + adduct	
	+40	Mainly adduct	
MeCOCOMe	−40, +20	Adduct	
$\mathrm{Ph_2C{=}CH_2}$	0	Adduct (to $\mathrm{CH_2}$ group)	

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[17] J. Cooper, A. Hudson, and R. A. Jackson, *J.C.S. Perkin II*, 1973, 1056.

[18] G. B. Watts and K. U. Ingold, *J. Amer. Chem. Soc.*, 1972, **94**, 491.

[19] A. J. Dobbs, B. C. Gilbert, and R. O. C. Norman, *J.C.S. Perkin II*, 1972, 2053 and references therein.

[20] E. Warhurst and A. M. Wilde, *Trans. Faraday Soc.*, 1971, **67**, 605; J. Oakes and M. C. R. Symons, *ibid.*, 1970, **66**, 10; L. Pasimeni, M. Brustolon, and C. Corvaja, *J.C.S. Faraday II*, 1972, 223 and references therein.

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

acetone and with diethyl oxalate is not complete, though the proportion of adduct is higher at higher temperatures. Ethyl trifluoroacetate does not react. With biacetyl the expected adduct is formed.

We note in passing that, not unexpectedly, tris(trimethylsilyl)silyl forms an adduct with 1,1-diphenylethylene.

Comparison between Silicon, Germanium, Tin, and Lead Radicals.—The experiments described above allow a reactivity order for a number of the carbonyl compounds to be established on the basis of the reactivity of the compounds towards the Group IVB radicals. The data from Table 6 [with differences between Me_2CO and $(CO_2Et)_2$ from Table 5] show that reactivity decreases in the order $MeCOCOMe > EtO_2CCO_2Et > Me_2CO > CF_3CO_2Me > HCO_2Me > CH_3CO_2Me$. The order diketones > oxalates > ketones > esters is to be expected on the basis of stabilization of the adduct radicals compared with the initial molecules. The order of esters $CF_3CO_2Me > HCO_2Me > CH_3CO_2Me$ may well reflect a polar contribution to the transition state: the CF_3 group will most readily stabilize negative charge developed during the reaction. The different ' cut-off ' point for reactivity of silicon compared with germanium, tin, and lead radicals is probably due to the fact that silicon forms stronger bonds to oxygen than do the other Group IVB elements: the present results suggest that perhaps the Ge–O and Sn–O bonds are not too different in strength, but that the Pb–O bond is weaker. Organotin radicals, unlike organosilicon or organogermanium radicals, react with α-diketones, oxalates, and quinones by electron transfer to give the corresponding organic radical anion. An interesting feature of the results is that the somewhat stabilized and sterically crowded tris(trimethylsilyl)silyl radical, which on these grounds might be expected to form somewhat weaker bonds to other groups, in fact displays a reactivity similar to the germyl and tin radicals.

TABLE 6

Comparison of reactivities of different $R_3M\cdot$ radicals with carbonyl compounds

	$Et_3Si\cdot$	$(Me_3Si)_3Si\cdot$	$Et_3Ge\cdot$	$Bu_3Sn\cdot$	$Me_3Pb\cdot$
MeCOCOMe	+	+	+	+	
$(CO_2Et)_2$	+	+,−	+,−	+	
Me_2CO	+	+,−	+,−	+	0
CF_3CO_2Et	+	−	−	0[a]	
HCO_2Me	+,−		−	0	
CH_3CO_2Me	−				

+, Adduct seen. −, $R_3M\cdot$ radical seen. 0, Nothing seen ($Bu_3Sn\cdot$ and $Me_3Pb\cdot$ are not expected to be visible, see text). [a] CF_3CO_2Me.

Thus the Group IVB radicals chosen show a reactivity in respect of addition to carbonyl compounds which can be explained in terms of metal–oxygen bond strengths, stabilization of the adduct radicals, electronegativity differences, and polar effects.

EXPERIMENTAL

A Varian E3 e.s.r. spectrometer with a variable temperature accessory was used for this work. Irradiation was by an Osram ME/D 250W high pressure mercury lamp, operated from a stabilized d.c. supply. The u.v. light was focused on to the cavity of the spectrometer by a quartz lens system: replacement of the 50% transmission grating on the front of the cavity by a copper plate with a 9·5 mm diameter circular hole, as described by Hammond and his co-workers,[22] gives better signals.

The ketones and other carbonyl compounds used were either commercially available, or were synthesized by standard methods.

Coupling Constants.—Data for new radicals, and for the radical anions observed during the work, are given below in Table 7. The appropriate hydrogen or fluorine atoms in the formulae have been italicized; multiplicities in accordance with these interpretations were observed in each case. Temperatures have been indicated where the coupling constants are markedly temperature dependent.

TABLE 7

Coupling constants (G) for new radicals

	α	β	γ	δ
$\mathit{H}\dot{C}(OSiMe_3)OC\mathit{H}_2CH_3$ (0 °C)	11·3		0·9	
(−100 °C)	12·7		1·0	
$C\mathit{H}_3\dot{C}(OSiEt_3)COC\mathit{H}_3$		15·6	1·7	
$C\mathit{H}_3\dot{C}(OSiEt_3)\cdot C\mathit{H}{=}C(O\mathit{H})C\mathit{H}_3$		14·8 * 2·9 †		13·4 * 1·4 †
$C\mathit{F}_3\dot{C}(OSiEt_3)OC\mathit{H}_3$ (40 °C)		18·1	1·3	
$C\mathit{F}_3\dot{C}(OSiEt_3)OC\mathit{H}_2CH_3$ (−20 °C)		18·0	1·4	
$C\mathit{F}_3C\mathit{F}_2\dot{C}(OSiEt_3)OC\mathit{H}_3$ (10 °C)		$27{\cdot}7^{F}$	$5{\cdot}2^{F}$ $1{\cdot}4^{H}$	
$C\mathit{F}_3C\mathit{F}_2C\mathit{F}_2\dot{C}(OSiEt_3)OC\mathit{H}_3$ (10 °C)		$27{\cdot}1^{F}$	$3{\cdot}5^{F}$ $1{\cdot}4^{H}$	$1{\cdot}4^{F}$
$C_3F_7CO\cdot O\cdot\dot{C}(OSiEt_3)C\mathit{F}_2CF_2CF_3$ (0 °C)		22·1		
$C\mathit{H}_3\dot{C}(OSiEt_3)O\cdot COC\mathit{H}_3$		15·5		0·45
$CH_3C\mathit{H}_2O\dot{C}(OSiEt_3)\cdot CO_2C\mathit{H}_2CH_3$			2·0	1·25
$C\mathit{H}_3\dot{C}(OSiEt_3)\cdot C\mathit{H}_2CO_2Et$		20·8 (CH_3) 13·6 (CH_2)		
$C\mathit{H}_3\dot{C}(OGeEt_3)\cdot COC\mathit{H}_3$		14·3	2·0	
$(C\mathit{H}_3)_2\dot{C}OGeEt_3$		19·8		
$CH_3C\mathit{H}_2O\dot{C}(OGeEt_3)\cdot CO_2\cdot C\mathit{H}_2CH_3$			2·1	1·4
$(C\mathit{H}_3)_2\dot{C}OSnBu_3$		19·1		
$[C\mathit{H}_3COCOC\mathit{H}_3]^{-\cdot}$		7·1		
$[CH_3C\mathit{H}_2O_2C\cdot CO_2C\mathit{H}_2CH_3]^{-\cdot}$			1·8	
$(C\mathit{H}_3)_2\dot{C}OSi(SiMe_3)_3$		20·0		
$CH_3C\mathit{H}_2O\dot{C}[OSi(SiMe_3)_3]CO_2C\mathit{H}_2CH_3$			1·9	1·3
$C\mathit{H}_3\dot{C}[OSi(SiMe_3)_3]COC\mathit{H}_3$		15·4	1·6	
$Ph\dot{C}(OSiEt_3)COPh$	3·0, quartet, *ortho*- and *para*-protons of one phenyl group 1·1, triplet, *meta*-protons of one phenyl group			
$[PhCOCOPh]^{-\cdot}$	1·0, quintet, *ortho*-protons of two phenyl groups 0·5, quintet, *meta*-protons of two phenyl groups 1·1, triplet, *para*-protons of two phenyl groups			
$[p\text{-}O\cdot C_6H_4\cdot O]^{-\cdot}$	2·4, quintet, from the four aromatic protons			
$Ph_2\dot{C}C\mathit{H}_2Si(SiMe_3)_3$	10·2, triplet, from the CH_2 group 3·1, septet, from *ortho*- and *para*-protons of two phenyl groups $1{\cdot}2_4$, quintet, from *meta*-protons of two phenyl groups			

* Quartet: assignments may be reversed. † Doublet: assignments may be reversed. ^{H} = Proton. ^{F} = Fluorine.

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