An E.S.R. Study of Some Reactions of Acylthiyl Radicals

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Summary U.v. photolysis of diacyl disulphides gives acylthiyl radicals [RC(O)S•] which react with alkenes,

trialkyl phosphites, and dialkyl sulphides to give adducts which have been detected by e.s.r. spectroscopy. ALTHOUGH acylthivl radicals $[RC(O)S_{\bullet}]$ (1) are thought to be involved in the homolytic chain reactions of thiocarboxylic S-acids with alkenes [equation (1)]¹ and of diacyl disulphides (2) with trialkyltin hydrides [equation (2)]² the reactivity of (1) has not been investigated extensively.

$$RC(O)SH + RCH=CH_2 \longrightarrow RCH_2CH_2SC(O)R$$
(1)

$$RC(O)SSC(O)R + R_3SnH \rightarrow R_3SnSC(O)R + RC(O)SH$$
 (2)

We report here a preliminary e.s.r. study of some reactions of (1), generated by u.v. photolysis of (2) in hydrocarbon solution [equation (3)].

$$\begin{array}{cc} & & & & & \\ RC(O)SSC(O)R & \longrightarrow 2RC(O)S \bullet & & (3) \\ & & & (2) & & (1) \end{array}$$

The diacyl disulphides (2; R = Et or Bu^{t}) were prepared from RC(O)Cl and Li_2S_2 , using the procedure recently developed by Gladysz et al.^{3†} E.s.r. spectra were recorded during continuous photolysis in the spectrometer cavity of cyclopropane solutions containing (2) and the compound whose reaction with (1) was to be studied.⁴ The spectroscopic parameters of the radicals detected are gathered in the Table. Photolysis of (2) alone in cyclopropane below of a cyclopropane solution containing (4),[†] di-t-butyl peroxide, and triethylsilane [equation (5)].⁶

$$Et_{3}Si_{\bullet} + EtC(O)SCH_{2}CH_{2}Br \longrightarrow$$

$$(4)$$

$$EtC(O)SCH_{2}CH_{2}_{\bullet} + Et_{3}SiBr$$

$$(5)$$

The low value of $a(2H_{\beta})$, which increases with increasing temperature, indicates that the most stable conformation of (3) is (5), in contrast to the staggered conformation (6) preferred by the acyloxy analogue.7



Addition of (1) to 2-methylpropene afforded only the spectrum of RC(O)SCH₂CMe₂ and no signal from the 2methylallyl radical (which would be formed by hydrogen abstraction from the alkene) was detectable.

TABLE. E.s.r. parameters of radicals produced by reactions of $(1; R = Et \text{ or } Bu^t)$ in cyclopropane

Radical detected	T/K	g-Factor	Hyperfine splittings ^a /G
EtC(O)SCH2CH2	179	2.0021	21·8 (2H _α); 13·3 (2H _β) ^b
$Bu^{t}C(O)SCH_{2}\dot{C}H_{2}$	179	$2 \cdot 0022$	21.8 (2H _{α}); 13.1 (2H _{β}) ^b
Bu ^t C(O)SCH ₂ CMe ₂	188	2.0030	22·0 (6H _β); 10·3 (2H _β) ^b
EtC(O)SP(OMe)3	158	2.0060°	886.3 (1P)°
Bu ^t C(O)SP(OMe) ₃	143	$2 \cdot 0064^{\circ}$	898·1 (1P)°
Bu ^t C(O)SSMe ₂	161	2.0140	3·6 (6H)
Bu ^t C(O)SŠEt ₂	159	2.0137	3·9 (4H)
Bu ^t C(O)SS(Et)Bu ^t	163	2.0143	4·9 (2H)
	Radical detected EtC(O)SCH ₂ \dot{C} H ₂ Bu ^t C(O)SCH ₂ \dot{C} H ₂ Bu ^t C(O)SCH ₂ \dot{C} Me ₂ EtC(O)S \dot{P} (OMe) ₃ Bu ^t C(O)S \dot{P} (OMe) ₃ Bu ^t C(O)S \dot{S} Me ₂ Bu ^t C(O)S \dot{S} Et ₂ Bu ^t C(O)S \dot{S} (Et)Bu ^t	Radical detected T/K EtC(O)SCH ₂ ĊH ₂ 179 Bu ^t C(O)SCH ₂ ĊH ₂ 179 Bu ^t C(O)SCH ₂ ĊMe ₂ 188 EtC(O)SP(OMe) ₃ 158 Bu ^t C(O)SP(OMe) ₃ 143 Bu ^t C(O)SŠMe ₂ 161 Bu ^t C(O)SSEt ₂ 159 Bu ^t C(O)SS(Et)Bu ^t 163	Radical detected T/K g-FactorEtC(O)SCH_2CH_2179 $2 \cdot 0021$ ButC(O)SCH_2CH_2179 $2 \cdot 0022$ ButC(O)SCH_2CH_2188 $2 \cdot 0030$ EtC(O)SP(OMe)_3158 $2 \cdot 0060^{\circ}$ ButC(O)SP(OMe)_3143 $2 \cdot 0064^{\circ}$ ButC(O)SSMe_2161 $2 \cdot 0140$ ButC(O)SSEt_2159 $2 \cdot 0137$ ButC(O)SS(Et)But163 $2 \cdot 0143$

^a Numbers of equivalent nuclei coupling shown in parentheses. ^b $a(2H_{\beta})$ increases with increasing temperature; for example, a(2H6) is 12.8 G at 160 K and 14.2 G at 216 K for Bu^C(O)SCH₂CH₂. ^c Calculated using the Breit-Rabi equation.

about 190 K gave rise to a weak single line spectrum (g 2.0240; peak-peak width ca. 2 G). This signal, which was also detected in the presence of alkenes or dialkyl sulphides (but not with trialkyl phosphites), may be due to the perthiyl radical RC(O)SS- formed by photochemical C-S cleavage of (2).5 No spectrum ascribable to (1) was detected. Above *ca.* 250 K, photolysis of $(2; R = Bu^{t})$ afforded a weak spectrum of the t-butyl radical.

Photolysis of (2) in the presence of ethylene afforded the spectrum of the appropriate β -acylthicalkyl radical (3) [equation (4)]. The assignment was confirmed by generating the radical (3; R = Et) independently during photolysis

$$RC(O)S \cdot + CH_2 = CH_2 \longrightarrow RC(O)SCH_2CH_2 \cdot$$
(4)
(3)

Acylthiyl radicals added to phosphorus(III) compounds to give phosphoranyl radicals [e.g. equation (6)], although it is not known at present whether these adducts have trigonal bipyramidal or tetrahedral (σ^* P-S) structures.⁸

$$RC(O)S \cdot + (MeO)_{3}P \longrightarrow RC(O)SP(OMe)_{3}$$
 (6)

Addition of (1) to dialkyl sulphides to give sulphuranyl radicals (7) also took place readily [equation (7)], providing an example of the expected similarity between (1) and CF₃S•.9

$$RC(O)S \cdot + R_2 S \longrightarrow RC(O)SSR_2$$
(7)
(7)

$$RS + R_2 S \rightleftharpoons RSSR_2$$
 (8)

† The disulphides (2; $R = Bu^{\dagger}$) and (2; R = Et) were purified by distillation (b.p. 75 °C at 0.03 Torr) and by h.p.l.c., respectively. Diacetyl disulphide was unsuitable on account of its poor solubility in hydrocarbons.

t Prepared by the method reported for MeC(O)SCH₄CH₄Br (L. Bauer, K. S. Suresh, and B. K. Ghosh, J. Org. Chem., 1965, 30, 949). Satisfactory spectroscopic data and elemental analysis were obtained for (4) (b.p. 50-52 °C at 0.03 Torr).

Under similar conditions with the less electrophilic alkylthiyl radical, the equilibrium (8) lies sufficiently far to the left that an e.s.r. spectrum of the sulphuranyl adduct cannot be detected.⁹ The g-factors of (7) (ca. 2.014) are close to those of CF_3SSR_2 , but lower than those (ca. 2.028) of radicals produced by radiolysis of thiols and disulphides in the solid state and assigned by Symons¹⁰ as RSSR₂ or

RSS. This suggests that the species with the higher g-factor should be identified as a perthivl radical.⁵ However, the g-factor of $XSSR_2$ could be significantly larger when X is a simple alkyl group than when X is a relatively electronegative CF3 or RC(O) group.

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¹G. Sosnovsky, 'Free Radical Reactions in Preparative Organic Chemistry,' Macmillan, New York, 1964, pp. 74-80. ²W. P. Neumann and J. Schwindt, *Chem. Ber.*, 1975, **108**, 1339.

- ² W. P. Neumann and J. Schwindt, Chem. Ber., 1975, 108, 1339.
 ³ J. A. Gladysz, V. K. Wong, and B. S. Jick, J.C.S. Chem. Comm., 1978, 838.
 ⁴ J. A. Baban, C. J. Cooksey, and B. P. Roberts, J.C.S. Perkin II, 1979, 781.
 ⁵ J. E. Bennett and G. Brunton, J.C.S. Chem. Comm., 1979, 62.
 ⁶ A. Hudson and R. A. Jackson, Chem. Comm., 1969, 1323.
 ⁷ D. J. Edge and J. K. Kochi, J. Amer. Chem. Soc., 1972, 94, 7695.
 ⁸ G. W. Eastland and M. C. R. Symons, J.C.S. Perkin II, 1977, 833.
 ⁹ J. R. M. Giles and B. P. Roberts, J.C.S. Chem. Comm., 1978, 623.
 ¹⁰ D. J. Nelson, R. L. Petersen, and M. C. R. Symons, J.C.S. Perkin II, 1977, 2005; 1978, 225.