

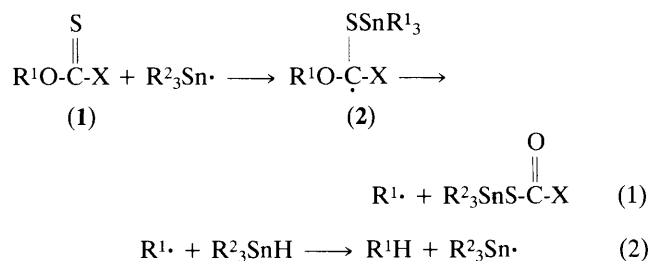
E.S.R. Identification of Alkoxythiocarbonyl Radicals as Possible Intermediates in Barton Deoxygenation of Alcohols

Philip J. Barker and Athelstan L. J. Beckwith*

Research School of Chemistry, Australian National University, G.P.O. Box 4, Canberra, A.C.T., Australia 2601

O-Alkyl *S*-methyl dithiocarbonates react with trimethyltin radicals to afford alkoxythiocarbonyl radicals which undergo slow β -fission to alkyl radicals and carbon oxysulphide.

Although reactions of trialkylstannanes with various thiocarbonyl compounds (1) are widely used for the deoxygenation of alcohols¹⁻³ this type of transformation has not yet been subjected to close mechanistic scrutiny. Nevertheless, it is usually assumed³ that a general free-radical chain mechanism applies [equations (1) and (2)] and that the yield of deoxygenated product depends critically on the rate of β -fission of the adduct (2) relative to that of competing processes such as direct hydrogen-atom transfer from stannane to (2). We now present evidence suggesting that reactions of dithiocarbonates (1); X = SMe, with trialkyltin radicals may follow an alternative pathway involving the intermediacy of alkoxythiocarbonyl radicals.



When a carefully purified[†] sample of the dithiocarbonate (1); X = SMe, R¹ = Me, was mixed with hexamethylditin and di-*t*-butyl peroxide in methylcyclohexane solvent and irradiated

[†] *O*-Alkyl *S*-methyl dithiocarbonates, when prepared by the usual procedure,¹ contain traces of dimethyl trithiocarbonate (MeSCS₂Me) which gives a very intense septet at *g* 2.0050 upon irradiation in the presence of hexamethylditin (ref. 4).

with u.v. light in the e.s.r. cavity a moderately strong quartet [$a(\text{H}) = 1.30 \text{ G}$][‡] was detected at *g* 2.0020. Since this signal was not observed when hexamethylditin was omitted from the mixture or when (1); X = SMe, R¹ = Me, alone in methylcyclohexane was irradiated, it is assigned to methoxythiocarbonyl radical formed by S_H2 attack of trimethyltin on the sulphide sulphur atom, equation (3).

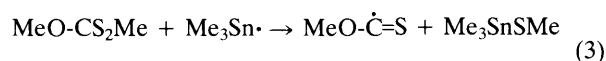


Table 1. E.s.r. parameters for radicals^a formed from dithiocarbonates and related precursors.

Precursor	Radical	<i>g</i> Factor	hfs (G)
(1); R ¹ = Me, X = SMe	MeO $\dot{\text{C}}\text{S}$	2.0020	1.30 (3H)
(1); R ¹ = Me, X = Cl	"	"	"
MeOCOCl	MeO $\dot{\text{C}}\text{O}$	2.0013 ^a	1.23 (3H) ^b
(1); R ¹ = <i>n</i> -hexyl, X = SMe	C ₆ H ₁₃ O $\dot{\text{C}}\text{S}$	2.0019	1.43 (2H)
(1); R ¹ = <i>n</i> -octyl, X = SMe	C ₈ H ₁₇ O $\dot{\text{C}}\text{S}$	2.0020	1.44 (2H)
(1); R ¹ = 2-octyl, X = SMe	C ₆ H ₁₃ CH(Me)O $\dot{\text{C}}\text{S}$	2.0019	0.5 (1H) ^c
CH ₂ OCSSCH ₂ (3)	Me ₃ SnSCH ₂ CH ₂ O $\dot{\text{C}}\text{S}$	2.0020	1.39 (2H)
(1); R ¹ = allyl, X = SMe	CH ₂ =CHCH ₂ \cdot	2.0026	14.8 (2H) 13.9 (2H)
Allyl-SCOSMe	"	"	4.1 (1H)

^a Generated by u.v. irradiation of degassed solutions of the dithiocarbonate, di-*t*-butyl peroxide, and hexamethylditin in methylcyclohexane at 243 K. ^b Ref. 5. ^c Incompletely resolved.

[‡] 1G = 10⁻⁴ T.

Similar treatment of other purified dithiocarbonates gave analogous signals. In each case the multiplicity of the signal and the low value of the hyperfine splitting (hfs) is consistent with the proposed structure (Table 1). The reaction of the cyclic dithiocarbonate (**3**) proceeds with ring fission. As expected, the value of $a(\text{H})$ for the radical MeOCS (1.30 G) is very similar to that of its oxygen analogue, MeOCO (1.43 G).⁵ The g factors, although sufficiently low to indicate a σ structure for alkoxythiocarbonyl radicals, are higher than those for similar alkoxy carbonyl radicals (*ca.* 2.0011)^{5,6} presumably because of the higher spin orbit coupling factor of sulphur as compared with oxygen. Further support for the proposed structures was obtained when the chloro compound (**1**); $\text{R}^1 = \text{Me}$, $\text{X} = \text{Cl}$, and the dithiocarbonate (**1**); $\text{R}^1 = \text{Me}$, $\text{X} = \text{SMe}$, were found to give identical spectra upon treatment with trimethyltin radicals. The observed spectra, however, were not intense enough to enable ^{13}C hyperfine coupling to be resolved.

When *O*-allyl *S*-methyl dithiocarbonate was irradiated with hexamethylditin and di-*t*-butyl peroxide only the allyl radical was detected. Presumably it arises by β -fission of $\text{CH}_2=\text{CHCH}_2\text{OCS}$ with elimination of carbon oxysulphide. *S*-Allyl *S*-methyl dithiocarbonate behaved similarly but in this case the mechanism is less clear since formation of allyl radicals by direct $\text{S}_{\text{H}2}$ attack of trimethyltin radicals upon sulphide sulphur is possible.

Although the allyl radical was the only β -fission product directly observed, the spin-trapping technique allowed the formation of other alkyl radicals to be detected. When tri-*n*-butylstannane was added to a mixture of (**1**); $\text{R}^1 = 2$ -octyl, $\text{X} = \text{SMe}$, perdeuterionitrosodurene,⁷ and methylcyclohexane at 353 K the spectrum of the 2-octyl radical spin-adduct was observed [$a(\text{N}) = 13.52$, $a(\text{H}) = 7.63$ G, $g = 2.0060$]. Similarly, other primary, secondary, and tertiary *O*-alkyl dithiocarbonates gave spectra of spin-adducts arising solely from the *O*-alkyl group. Nitrosodurene, 2-methyl-2-

nitrosopropane, and phenyl-*t*-butyl nitron could be used effectively as spin-traps in these systems.

The identification of alkoxythiocarbonyl radicals as primary products of the reaction between *O*-alkyl *S*-methyl dithiocarbonates and trimethyltin radicals suggests that the Barton deoxygenation procedure may involve the same intermediates [equations (4) and (5)]. The observation¹ that COS is liberated



during the reaction with stannane and that the crude product shows no carbonyl absorption in the infrared supports this hypothesis.

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