# Photodecomposition Modes of *S*-Alkyl Thiocarboxylates

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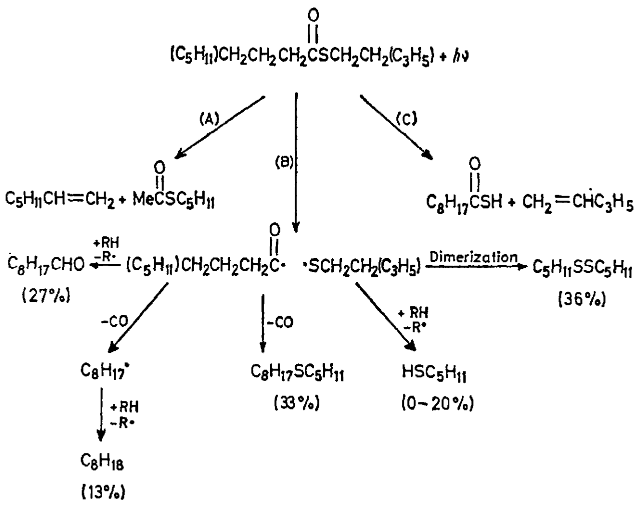
*Summary* In contrast to the type II photoelimination reaction observed in the closely related *S*-alkyl thiocarbonates, *S*-alkyl thiocarboxylates photodecompose by sulphur–acyl bond cleavage.

As an extension of studies related to the chemical and physical characteristics of carboxylate ester excited states,[1] photochemical studies of the previously uninvestigated *S*-alkyl thiocarboxylate esters were undertaken. In contrast to the photochemistry observed for alkyl carboxylates,[1] dialkyl thiocarbonates,[2] and certain alkyl thioesters,[3] the photochemical results indicate that decomposition of *S*-alkyl thiocarboxylates involves initial sulphur–acyl bond cleavage.

$RCH_2C(O)S[CH_2]_4Me$
(**1**) **a**; $R = [CH_2]_6Me$
**b**; $R = Me$
**c**; $R = H$

Degassed alkane solutions of (**1a**), (**1b**), and (**1c**) were photolysed with 254 nm light. The quantitative results for (**1a**) are shown in the Scheme. The results for (**1b**) and (**1c**) were qualitatively the same. In general, the products accounted for $< 100\%$ of the ester decomposed. As expected, the disulphide decomposed after a long photolysis time under the reaction conditions used.[4] Cyclohexane (1·0 M) was added in some cases as a radical trap giving as much as 47% cyclohexyl pentyl sulphide.

Products of the type II elimination reaction on the carbon side of the carbonyl group, path A, in ester (**1a**) were very carefully sought. Although peaks in the gas chromatograms corresponding to heptane and (**1c**) were observed, the yields were extremely low, *ca.* 0·4% in each case.† Type II elimination on the other side of the carbonyl group, path C, also was essentially absent as indicated by $<0·4\%$ but-1-ene from (**1a**). In addition, during the photolysis of ester (**1c**), no thioacetic *S*-acid was detected and $<0·02\%$ *S*-cyclohexyl ethanethioate was present when cyclohexene was added as a trapping agent.‡[5]



Scheme. 38% *of the starting ester was decomposed. Yields are based on decomposed ester.*

The major products can all be explained by a simple cleavage of the sulphur–acyl bond followed by free-radical reactions, path B. Consistent with this explanation is the

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† Due to low yields of these products, identification was not carried beyond the stage of retention time comparisons.

‡ We suspected that the thioacetic *S*-acid might be disappearing by the well known free-radical addition of thioacids to olefins, and cyclohexene was added to trap the acid as *S*-cyclohexyl ethanethioate.

47% yield of cyclohexyl pentyl sulphide observed when cyclohexene was added. Although carbon–carbon bond cleavage $\alpha$ to the carbonyl group could explain some of the products, this seems an unnecessary complication especially in the light of the relatively high yield of nonanal which requires sulphur–acyl bond cleavage. In general, changes in structure had little effect on the modes of decomposition or their relative importance.

Why saturated *S*-alkyl thiocarboxylates do not undergo the type II elimination with any degree of efficiency is not obvious.[6] Despite speculation to the contrary,[7] a weak transition evident in the u.v. absorption spectra of *S*-alkyl thiocarboxylates was observed near 265 nm indicative of the requisite $n,\pi^*$ lowest energy singlet. In addition, though formation of the thiyl radical is easy this must also be a competing process in the photochemistry of dialkyl thiocarbonates.[2]

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[6] Although aromatic thiocarboxylates undergo the sulphur–acyl bond cleavage efficiently, this is not in contrast with but rather identical to the processes observed in the corresponding oxygen compounds: see J. R. Grunwell, *Chem. Comm.*, 1969, 1437; E. L. Loveridge, B. R. Beck, and J. S. Bradshaw, *J. Org. Chem.*, 1971, **36**, 221.

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