Novel Dethioacetalisation by Photolysis

By Thomas T. Takahashi*

(*Department of Chemistry, The Jikei University School of Medicine, Kokuryo, Chofu, Tokyo* 182, *Japan*)

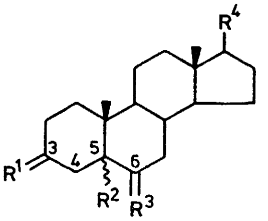
and Cyprian Y. Nakamura and James Y. Satoh

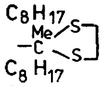
(*Department of Chemistry, Rikkyo University, Nishi-Ikebukuro, Tokyo* 171, *Japan*)

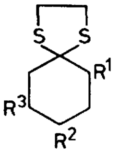
Summary Thioacetals were converted into the parent ketone by irradiation with a Hg lamp in an oxygen atmosphere.

Thioacetals are important as protecting groups in organic synthesis.[1] However, because of their relative stability to base and acid, it is difficult to regenerate the parent carbonyl compounds. Various methods have been studied to overcome this problem, *e.g.*, use of metal salts[2] and acidic conditions,[3] conversion into reactive sulphonium salts,[4] and oxidation to a labile disulphoxide and disulphone.[5] However, dethioacetalisation by photochemical means has not been reported.

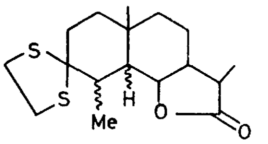
In a study of the photolysis of sulphur-containing steroids we discovered that dethioacetalisation occurred upon photoirradiation, resulting in the formation of the parent ketone. It was also found that this method was applicable to ethylene and dibenzyl dithioacetal derivatives.



	R^1	R^2	R^3	R^4
(1)	$-SCH_2CH_2S-$	α-H	H_2	C_8H_{17}
(2)	$-SCH_2CH_2S-$	Δ^4-compound	H_2	C_8H_{17}
(3)	α-H, β-AcO	Δ^5- compound		
(4)	$-SCH_2CH_2S-$	β-H	H_2	C_8H_{17}
(5)	α-H, β-AcO	α-H	$-SCH_2CH_2S-$	C_8H_{17}
(6)	$(PhCH_2S)_2$	α-H	H_2	C_8H_{17}
(7)	$-SCH_2CH_2O-$	α-H	H_2	C_8H_{17}



(8) $R^1 = R^2 = R^3 = H$
(9) $R^1 = Me, R^2 = R^3 = H$
(10) $R^1 = R^3 = H, R^2 = Bu^t$
(11) $R^1 = Pr^i, R^2 = H, R^3 = Me$



(12)

In a typical experiment, a mixture of 5α-cholestan-3-one ethylene dithioacetal (**1**) (200 mg), benzophenone (394 mg), and hexane (200 ml) was irradiated with a high-pressure Hg lamp mounted in a Pyrex immersion tube for 3·5 h in a stream of oxygen at room temperature to give 5α-cholestan-3-one (77%). Results for other thioacetals are in the Table.

Table

Thioacetal	Conc./mM	Time/h	% Yield of ketone[a]	Method[b]
(**1**)	2·16	3·5	77	A
(**2**)	2·17	2·0	57	A
(**3**)	2·79	2·0	65	D
(**4**)	2·16	4·0	75	A
(**5**)	1·92	2·0	68	A
(**6**)	0·32	3·0	80	C
(**7**)	2·24	3·0	61	A
(**8**)	5·74	4·5	65	B
(**9**)	5·31	2·5	70	C
(**10**)	4·34	5·5	60	B
(**11**)	4·34	4·5	87	B
(**12**)	3·99	2·0	60	D

[a] Yield by g.l.c. analysis based on thioacetal. [b] A: hexane solvent, 5 mol. equiv. benzophenone, 100 W high-pressure Hg lamp; B: hexane solvent, 2 mol. equiv. benzophenone, 100 W high-pressure Hg lamp; C: acetone solvent, no benzophenone, 100 W high-pressure Hg lamp; D: hexane solvent, no benzophenone, 30 W low-pressure Hg lamp.

The resulting ketones were isolated by preparative t.l.c. and column chromatography on silica-gel, and identified by comparison (m.p., i.r., n.m.r., and g.l.c. retention times) with authentic samples.

This method affords a new simple operation for dethioacetalisation; it differs from conventional methods in that neutral conditions are used. It is particularly noteworthy that this photolytic method was successfully applied to the dethioacetalisation of the ethylene dithioacetal derivative of tetrahydrosantonine (**12**); we have found that attempted dethioacetalisation by the conventional method[2a] failed. The new method is useful in cases where an acid- and base-sensitive unit (lactone, ester, *etc.*) is present in the substrates. Moreover, dethioacetalisation itself is a novel reaction in the field of photochemistry.

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