

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 salts² 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.

In a typical experiment, a mixture of 5 α -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 5 α -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

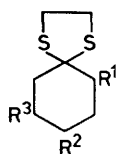
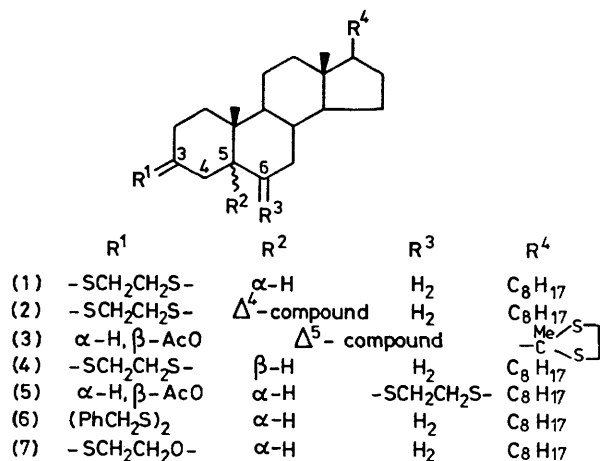
^a Yield by g.l.c. analysis based on thioacetal. ^b A: hexane solvent, 5 mol. equiv. benzophenone, 100 W high-pressure Hg lamp; B: hexane solvent, 2 mol. equiv. benzophenone, 100 W high-pressure Hg lamp; C: acetone solvent, no benzophenone, 100 W high-pressure Hg lamp; D: hexane solvent, no benzophenone,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

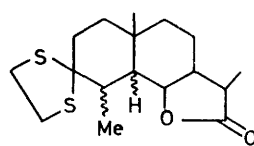
This method affords a new simple operation for dethioacetalisation; it differs from conventional methods in that neutral conditions are used. It is particularly noteworthy that this photolytic method was successfully applied to the dethioacetalisation of the ethylene dithioacetal derivative of tetrahydrosantonine (**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.

We thank Professors Jisaku Kuroda, Machiko Tozawa, and Tsunetaka Kushimoto of the Jikei University School of Medicine for their interest and encouragement.

(Received, 8th June 1977; Com. 557.)



- (8) R¹ = R² = R³ = H
 (9) R¹ = Me, R² = R³ = H
 (10) R¹ = R³ = H, R² = Bu^t
 (11) R¹ = Prⁱ, R² = H, R³ = Me



(12)

¹ D. Seebach, *Synthesis*, 1969, 17.

² (a) K. Narasaka, T. Sakashita, and T. Mukaiyama, *Bull. Chem. Soc. Japan*, 1972, **45**, 3724; (b) T. L. Ho, H. C. Ho, and C. M. Wong, *J.C.S. Chem. Comm.*, 1972, 791; (c) D. Gravel, C. Vaziri, and S. Rahal, *ibid.*, p. 1323; (d) T. L. Ho and C. M. Wong, *Canad. J. Chem.*, 1972, **50**, 3740.

³ G. Karmas, *Tetrahedron Letters*, 1964, 1093.

⁴ T. Oishi, K. Kamemoto, and Y. Ban, *Tetrahedron Letters*, 1972, 1085.

⁵ P. R. Heaton, J. M. Midgley, and W. B. Whalley, *Chem. Comm.*, 1971, 750.