Tetrahedron Letters,Vol.29,No.43,pp 5471-5474,1988 0040-4039/88 $3.00 + .00
Printed in Great Britain Pergamon Press plc

A NEW PROCEDURE FOR DETHIOACETALIZATION

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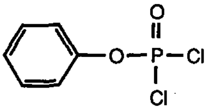
Summary: A simple procedure has been developed for the conversion of thioacetals to the corresponding carbonyl compounds using the combination of phenyl dichlorophosphate, dimethylformamide and sodium iodide.

Thioacetal is a useful protecting group which is easy to prepare and is stable under various commonly encountered reaction conditions.[1] It also serves as an excellent acyl carbanion equivalent in synthesis.[2] A number of methods are available for the conversion of thioacetals to the parent carbonyl compounds.[1,2] These methods often require drastic conditions or toxic reagents such as mercury salts. In some cases mild conditions apply, but multistep operations are needed. Consequently, the synthetic application of the thioacetal functionality is somewhat hampered. In this communication, we wish to describe a simple, direct method which effects dethioacetalization using mild, virtually neutral conditions.

Recently we have successfully applied the combination of phenyl dichlorophosphate (PDCP) (**1**) and sodium iodide to effect the conversion of acetals to the corresponding carbonyl compounds,[3] presumably via the pathway outlined in Scheme 1. Based on these results, it is conceivable that treatment of thioacetals with PDCP in the presence of sodium iodide could lead to the formation of thiones. In practice however, when thioacetal **2** derived from acetophenone was treated with the above reagents in acetonitrile at room temperature, the starting material was virtually intact. When the reaction was carried out at reflux temperature, a complex mixture was produced. Interestingly, with the addition of dimethylformamide (DMF),[4] the starting material was consumed within 2 h at room temperature and, to our delight, a single compound was formed. Unexpectedly, the compound was identified to be acetophenone. Based on this observation, a general procedure has been developed for the conversion of thioacetals to the corresponding carbonyl compounds employing the combination of PDCP, sodium iodide and DMF.

A typical experiment is as follows. To 2-methyl-2-nonyl-1,3-dithiolane (**3**) (232 mg, 0.94 mmol) and sodium iodide (630 mg, 4.2 mmol) in dry acetonitrile (3 mL) under an atmosphere of argon, was added PDCP (0.16 mL, 1.07 mmol). After a few min, DMF (0.08 mL, 1.03 mmol) was added. The



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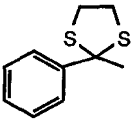

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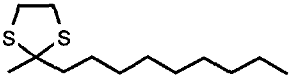

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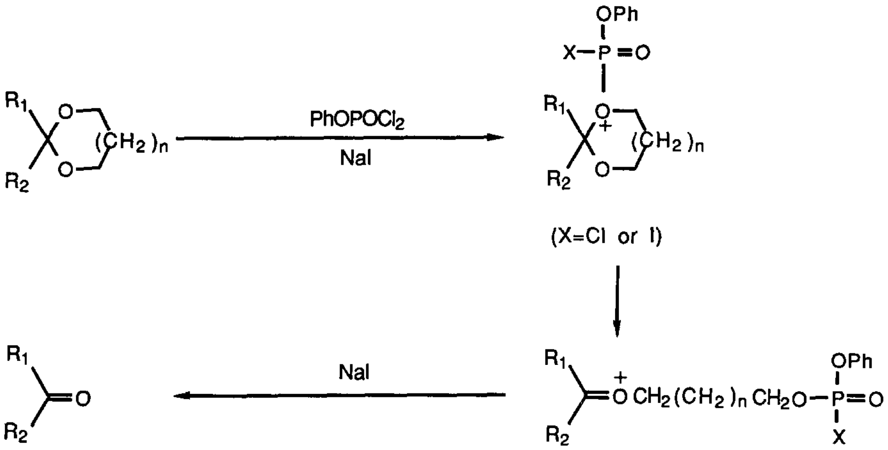
Scheme 1

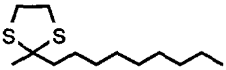
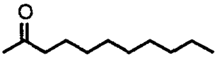
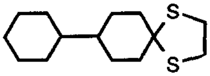
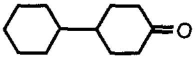
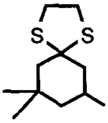
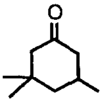
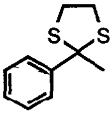
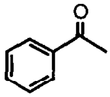
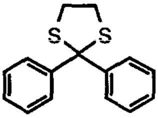
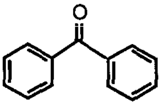
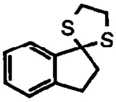
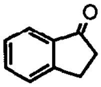
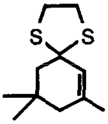
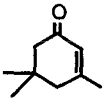
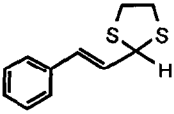
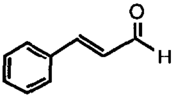


apparatus was then wrapped in aluminum foil. After stirring at room temperature for 5 h, the reaction mixture was concentrated and then subjected to column chromatography on silica gel. Elution with 20% diethyl ether in petroleum ether gave 2-undecanone (151 mg, 94% yield).

As illustrated in Table 1 which summarizes the results obtained for several compounds examined, the procedure is applicable not only to aliphatic thioacetals (entries 1-3), but also to aromatic (entries 4-6) and allylic ones (entries 7 and 8). The formation of the aldehyde carbonyl is equally effective (entry 8). Although several products were isolated in only modest yield, in all cases the reaction proceeded cleanly, and the desired compound was formed as the only detectable product by thin-layer chromatography.

The following observations are also noteworthy. (1) As mentioned previously, under similar conditions the reaction of thioacetal **2** did not occur in the absence of DMF. (2) In the absence of sodium iodide, the reaction of thioacetal **3** with DMF and PDCP was found to be extremely slow. After 70 hr,only traces of 2-undecanone was detected. (3) The use of phosphorus oxychloride (in place of PDCP), DMF and sodium iodide was also

Table 1. Transformation of thioacetals to carbonyl compounds

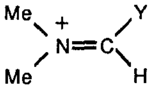
Entry	Thioacetal	Time (h)[a]	Product	% Yield[b]
1		1		94
2		17		77
3		2		90
4		1		71
5		10		92
6		2		76
7		2		73
8		2		73

[a] All reactions were carried out at room temperature, using 1.1 equiv. of $PhOPOCl_2$, 1.1 equiv. of $HCONMe_2$, and 4.5 equiv. of NaI.

[b] Yields given are for isolated products, and have not yet been optimized.

effective in the dethioacetalization of compound **3**. However, the yield of 2-undecanone was inferior. Again in this case, the reaction was extremely slow when sodium iodide was omitted; only traces of the product was detected after 24 h.

The mechanism of the reaction remains to be determined. However, it is likey that an intermediate such as **4**[7] similar to the Vilsmeier-Haack reagent[8] serves as the activating agent. More importantly, regardless of the pathway in which the reaction proceeds, it is clear that the combination of PDCP, DMF and NaI is necessary to efficiently promote the transformation.[9]



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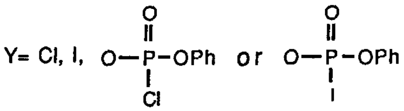

$Y = Cl, I, O{-}P(=O)(Cl){-}OPh$ or $O{-}P(=O)(I){-}OPh$

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9. We are grateful to the Natural Sciences and Engineering Research Council of Canada and the University of Alberta for financial support.

(Received in USA 16 June 1988)