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A NEW METHOD FOR THE DEPROTECTION AND REDUCTION OF DITHIOACETALS

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Reductive desulfurization of aromatic ketone dithioacetals **1** was achieved by the reaction of **1** with a mild reagent, P_2I_4, in dichloromethane. On the other hand, treatment of **1** with P_2I_4 in acetic anhydride or chloroform selectively gave deprotected ketones.

Dithioacetals have been not only useful as a protecting group but also important as a synthon of carbonyl compounds. Remarkable efficiency in P_2I_4 mediated cleavage of phenolic acetals[1] prompted us to apply the method to transformation of dithioacetals. We report herein that treatment of dithiolanes having aromatic substituents **1** with P_2I_4 selectively gave benzophenone type **2** or diphenylmethane type products **3** under the mild conditions. The reaction of **1a** (R = R' = Ph) with P_2I_4 in Ac_2O, $CHCl_3$, and CCl_4 respectively gave benzophenone (**2a**) in 43 - 80% yields (Table 1). In contrast, diphenylmethane (**3a**) was obtained by the same reaction carried out in CH_2Cl_2.[2]

A typical procedure is as follows. 2,2-Diphenyl-1,3-dithiolane (**1a**) (73 mg, 0.30 mmol) was allowed to react with P_2I_4 (172 mg, 0.30 mmol) in Ac_2O (4 ml) at room temperature for 7 h under a nitrogen atmosphere. After removal of Ac_2O under the reduced pressure, ether and a sat. aqueous solution of $NaHSO_3$ were added. The ether extracts were concentrated and purified by preparative TLC to give **2a** (80% yield).

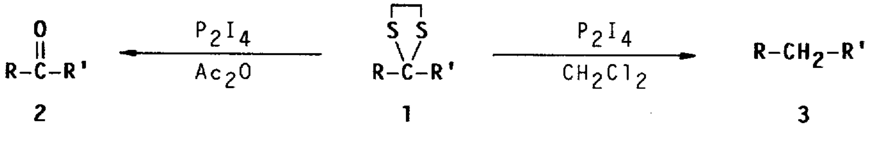

Table 1. Reaction of 2,2-Diphenyl-1,3-dithiolane with P_2I_4[a)]

Solvent	Time	Yield	**2a**:**3a**	Recovery of **1a**
	h	%		%
Ac_2O	7	80	100: 0	0
$CHCl_3$	24	62	100: 0	10
CCl_4	30	43	100: 0	19
Benzene	23	89	57:43	2
Cyclohexane	30	45	27:73	27
CH_2Cl_2	20	80	27:73	0

a) Dithiolane **1a**/P_2I_4 = 1/1 (mol/mol), rt.

Table 2. Reaction of Dithiolanes with P_2I_4[a)]

Dithiolane	1		Solvent	Additive	Time	Yield	2 : 3
R	R'				h	%	
Ph	Ph	**1a**	CH_2Cl_2	D_2O	6	93	9:91
4-MeO-C_6H_5	Ph	**1b**	Ac_2O	–	7	72	100: 0
			CH_2Cl_2	–	20	74	23:77
			CH_2Cl_2	H_2O	6	93	10:90
4-Me-C_6H_5	Ph	**1c**	Ac_2O	–	7	88	100: 0
			CH_2Cl_2	–	27	73	32:68
			CH_2Cl_2	H_2O	8	86	6:94
4-Cl-C_6H_5	Ph	**1d**	Ac_2O	–	7	68	100: 0
			CH_2Cl_2	–	20	81	33:67
			CH_2Cl_2	H_2O	8	90	11:89
4-MeO-C_6H_5	n-C_4H_9	**1e**	Ac_2O	–	9	53	100: 0
			CH_2Cl_2	–	45	21[b)]	100: 0

a) Dithiolanes **1**/P_2I_4 = 1/1 (mol/mol); additive, 1 mol eq.; rt.
b) Recovery of **1e**: 50%.

As shown in Table 2, dithiolanes with two aromatic substituents were transformed into **2** and **3** in good yields, while the less reactive dithiolane **1e** having an aliphatic substituent gave only **2e** in low yields.

Although the reason for the different solvent effect between Ac_2O and CH_2Cl_2 is still unclear, it is interesting that treatment of **1a** with P_2I_4 in CD_2Cl_2 followed by workup with D_2O failed to give deuterated diphenylmethane. On the other hand, reduction of **1a** with P_2I_4 in CH_2Cl_2 in the presence of D_2O (1 mol eq.) gave **3a** (85% yield; deuterium content 73%). The results suggest the presence of a trace amount of the proton source such as water in CH_2Cl_2.[3] Furthermore, there was an effect of H_2O addition on the reduction reaction. Selectivity and yields of **3** in the presence of H_2O (1 mol eq.) were much higher than those in the absence of H_2O.

In order to apply this method to the transformation of oxathiolane, 2,2-diphenyl-1,3-oxathiolane (**4**) was stirred with P_2I_4 in Ac_2O at room temperature for 10 h to give **2a** (76% yield), however, treatment of **4** with P_2I_4 in CH_2Cl_2 gave a complex mixture. Further application of this method is in progress.

References and Notes

1. H. Saimoto, Y. Kusano, and T. Hiyama, Tetrahedron Lett., **27**, 1607 (1986).
2. Solvents were dried by the reported methods: D. D. Perrin, W. L. F. Armarego, and D. R. Perrin, "Purification of Laboratory Chemicals," 2nd ed, Pergamon Press, Oxford (1980).
3. The origins of protons in the P_2I_4 reduction of thioketones was attributed to a trace of water, see: H. Suzuki, H. Tani, and S. Takeuchi, Bull. Chem. Soc. Jpn., **58**, 2421 (1985). See also, H. Suzuki, H. Tani, H. Kubota, N. Sato, J. Tsuji, and A. Osuka, Chem. Lett., **1983**, 247.

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