Reactions of P-Cl Compounds in presence of SmI₂.

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Abstract: Conversion of P-Cl to P-H and P-C bonds are induced by SmI_2 in mild conditions. Especially phosphines oxides and sulfides are obtained in good yields.

We described preparation of SmI₂ in THF solutions in 1977¹ and investigated its uses as a powerful reducing agent². We reported the deoxygenation of epoxides and sulfoxides, the reductions of alkyl halides, double bonds and carbonyl compounds. SmI₂ mediates Barbier-type reactions, Reformatsky reactions², and couplings of acid chlorides³⁻⁵. SmI₂ chemistry, which was developed by various groups, is summarized in some review articles⁶⁻⁹. Inanaga et al. found that several reactions of SmI₂ such as reduction of halides, Barbier reactions and deoxygenation of α -oxygenated esters were strongly accelerated by addition of a few equivalents of HMPA^{10,11}.

At the present time SmI_2 has been only scarcely used in phosphorus chemistry. $Sm(O=PMePh_2)_4I_2]I$ has been prepared by treating SmI_2 with excess isopropanol in THF and subsequently with $O=PPh_2Me^{12}$. There was no reduction of the phosphine oxide, as already noticed with $O=PPh_3^2$. Triphenyl phosphine is obtained only by using SmI_2 in the presence of HMPA in refluxing THF¹³. We report herein the behaviour of P-Cl bonds towards SmI_2 .

We have recently found that certain P-Cl compounds were smoothly converted into the corresponding P-H compound at room temperature by the action of SmI_2 .



Results are collected in Table I. In a typical procedure a solution of P-Cl compound (2 mmol) in THF (2 mL) was added dropwise to a stirred solution of SmI_2 .

(0.1 M, 40 mL, 4 mmol) in THF at room temperature under Ar. The reaction continues until disappearance of the typical blue colour of SmI₂. Hydrolysis with 0.1 N HCl followed by ether extraction and evaporation of the solvent gave a crude product which was purified by column chromatography or recrystallization. Reduction of diphenylchlorophosphine oxide and sulfide occurs rapidly leading respectively to 1 and 2 in high yields. With O-ethyl phenylphosphorochloridothionate (entry 4) the reaction is slower. The introduction of two ethoxy substituents into the starting P-Cl compound results in a drastic decrease of the yield of the product (entries 5 and 6).

Entry	R ¹	R ²	х	ta	Product	Yield(%)	
1	Ph	Ph	0	35 min	1	75 ^b	
2	Ph	Ph	S	40 min	2	89	
3	Ph	EtO	0	7 days	3	0 ^c	
4	Ph	EtO	S	48 hr	4	91	
5	EtO	EtO	0	3 hr ^d	5	10 ^c	
6	EtO	EtO	S	7 days	6	20 ^e	

Table I.: Conversion of $(\mathbb{R}^1)(\mathbb{R}^2)\mathbb{P}(X)$ -Cl to $(\mathbb{R}^1)(\mathbb{R}^2)\mathbb{P}(X)$ -H using Sml₂ in THF.

^a Reaction time at room temperature (except for entry 5) with a molar ratio of 1:2, $R^1R^2P(X)CI:$ SmI₂. For molar ratio of 1:1 the starting P-Cl compounds were largely recovered. ^b Coupling product, Ph₂P(O)P(O)Ph₂ was obtained as a by-product in 7% yield. ^c The formation of polymers was observed. ^d Under reflux. ^e The starting P-Cl compound was recovered in 65% yield.

In order to establish the stereochemical course of the reaction leading to 4 (entry 4) both enantiomers of O-ethyl phenylphosphorochloridothionate 7 were prepared by modifying the method of Ohkawa et al.¹⁴. The results for the reaction with SmI_2 are listed in Table II. The absolute configurations and enantiomeric excesses of the products were determined by chemical transformations.

$$CI \int_{OEt}^{S} P_{h} \xrightarrow{i) Sml_{2}/rt} H \int_{OEt}^{S} P_{h}$$

$$(B)-(-)-7 \qquad (S)-(+)-4$$

7	[α] _D (7) ^a	ee%	ťp	4 C	[α] _D (4) ^a	ee%	4	
(R)-(-)	-72.2°	90	48hr	83	+3.8°	20	(S)	-
(R)-(-)	-72.0°	90	60hr	87	+0.9	4.5	(S)	
(S)-{+}	+70.5°	88	48hr	80	-3.6°	19	(R)	
(S)-(+)	+73.0°	91	60hr	85.3	±0.0	-		

Table II : Reduction of optically active 7 by SmI_2 in THF.

a $[\alpha]_D$ (CDCl₃); b t: reaction time at room temperature in presence of 2 mol.eq of Sml₂: c isolated yield (%).

The absolute configuration of the starting O-ethyl phenylphosphorochloridothionate 7 was based on the literature 15. The enantiomeric excesses (Table II) were estimated by comparison with the reported $[\alpha]_D$ value. The absolute configuration of O-ethyl phenylphosphinothionate 4 was established by the following chemical transformation. Enantiomerically enriched (-)-3 was prepared by reacting ethyl chloroformate with the phenylphosphinium salt which was derived from phenylphosphinic acid and (-)-N-methylephedrine¹⁶. The absolute configuration and enantiomeric excess of (-)-3 were based on the reported data 17^{-19} . Thiation of (-)-3 (10.8% ee) using Lawesson's reagent gave (-)-4 in 44% yield²⁰. It is known that this type of thiation proceeds with retention of configuration²¹. Therefore, (-)-4 has (R)- configuration.



The data of Table II show that the reaction proceeds with partial retention of configuration (after 48 hr) or with complete racemization (after 60 hr). This was unexpected since there are examples of stereochemical stability of $EtO(Ph)P=O^{-}$ at asymmetric phosphorus^{18,19} and more detailed studies are needed to elucidate this result.

Besides the reduction reactions, SmI_2 can be used to achieve couplings of P-Cl compounds with benzyl chloride or methyl iodide. A mixture of diphenyl chlorophosphine oxide or sulfide (2 mmol) and benzyl chloride or methyl iodide (2 mmol) in THF (2 mL) was added dropwise at room temperature under Ar to a stirred solution of SmI_2 (0.1 M, 40 ml, 4 mmol) in THF. After 1 hr the reaction mixture has

turned yellow and was quenched and purified as indicated above. Phosphines oxides 8 and 9 and phosphine sulfide 10 were isolated in good yields.

> Ph P + RX' Sml₂/rt 8 RX' = CICH₂Ph X = O55% RX' = CH₃I X≖O 74% 9 RX' = CHal X = S71% 10

The first results for the preparation of phosphine oxides and sulfides using reduction and coupling reactions mediated by SmI2 are promising. It is particularly striking that mixed coupling exclusively occurs with benzyl chloride which is known to be transformed in dibenzyl by Sml_2^2 . A convenient one pot preparation of tertiary phosphines seems to be possible. Further studies for selective conversion of some P-Cl compounds to P-Sm and P-H compounds as well as formation of P-C bonds using divalent samarium are currently in progress especially for synthesis of P(III) compounds.

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