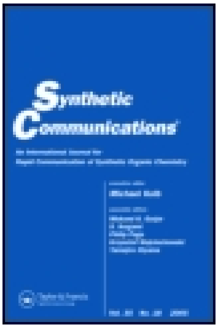

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Tellurium Tetrachloride as an Efficient Chlorinating Agent for Di- or Trialkyl Phosphites: Novel Synthesis of Dialkyl Chlorophosphates

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TELLURIUM TETRACHLORIDE AS AN EFFICIENT CHLORINATING AGENT FOR DI- OR TRIALKYL PHOSPHITES: NOVEL SYNTHESIS OF DIALKYL CHLOROPHOSPHATES

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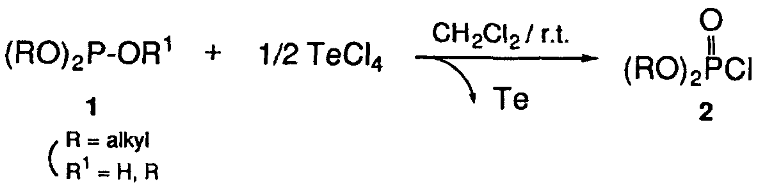
ABSTRACT : Various dialkyl chlorophosphates are prepared by the reaction of $TeCl_4$ with di-or trialkyl phosphites in good yields.

Organic synthesis using tellurium tetrachloride is current interest and is growing.[1] Interestingly, tellurium(IV) chloride shows ambident electrophilic reactivity against various nucleophiles to cause telluration or chlorination. When tellurium(IV) chloride reacts with carbanion such as Grignard or alkyl lithium reagents, telluration occurs to give di- or tetraalkyl tellurium.[2] And, in the case of alcohols and electron rich aromatic systems, telluration occurs at oxygen and *para*-position of aromatic ring respectively.[3,4] However, chlorination has not been nearly reported except for the reaction of anthracene which gives 9-chloroanthracene.[5]

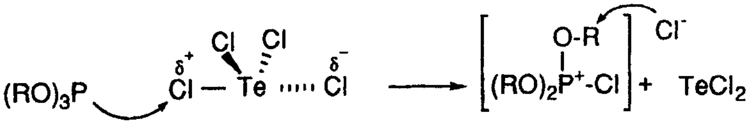


Scheme

Recently we observed that the reaction of tellurium(IV) chloride with di- or trialkyl phosphites affords dialkyl chlorophosphates with the black precipitation of tellurium metal (Scheme).

In the present paper, we wish to report a new feature of tellurium tetrachloride as a mild and efficient chlorinating agent for various alkyl phosphites. The typical experimental procedure is as follows: To a solution of $TeCl_4$(148 mg, 0.55 mmol) in 5 ml of CH_2Cl_2 was added dropwise a solution of triethyl phosphite(166 mg, 1.0 mmol) in 5 ml of CH_2Cl_2 under nitrogen atmosphere at room temperature. As reaction proceeded, the mixture became black due to precipitation of tellurium metal. After stirring for about 30 min, the solution was filtered through Celite and the filtrate was concentrated to give crude diethyl chlorophosphate. The crude product was purified by silica gel column chromatography using EtOAc/n-Hexane (1:2) as eluent in 83 % yield.[6] The results of reactions with a variety of alkyl phosphites are listed in Table.

Usual aliphatic di- or trialkyl phosphites are easily converted to corresponding dialkyl chlorophosphates in good yield(entry 1-9). The reaction may proceed by the attack of phosphorus center of tervalent alkyl phosphite on the positive chlorine of $[TeCl_3]^{\delta+}Cl^{\delta-}$ which is the partially ionized form of $TeCl_4$ in solution (Figure).[7] Initially formed $TeCl_2$



Figure

Table . Preparation of Dialkyl chlorophosphates

Entry	1		time	2
	R	R^1	(min)	Yield(%)[a]
1[b]	Me	H	60	85
2[b]	Et	H	60	90
3[b]	i-Pr	H	60	87
4[b]	n-Bu	H	60	85
5[b]	$PhCH_2$	H	60	50
6	Me	Me	30	88
7	Et	Et	30	83
8	i-Pr	i-Pr	30	75
9	n-Bu	n-Bu	30	80
10	Ph	Ph	60	-[c]

[a] Isolated yield based on alkyl phosphite; [b] 1 eq. of Et_3N was added for trapping the formed HCl; [c] $(PhO)_3P{=}O$ was obtained in 90 % yield.

disproportionates into Te and $TeCl_4$ which is consumed in the reaction. In the case of triphenyl phosphite, however, triphenyl phosphate was obtained by hydrolysis of assumed intermediate, $(PhO)_3PCl_2$, because of the difficulty of nucleophilic displacement at aryl carbon (entry 10).

Similar treatment of tellurium tetrachloride with sodium diethyl phosphite gave a large amount of dimerized side product, tetraethyl hypophosphate, $(EtO)_2P(O)OP(OEt)_2$. It might be formed by the reaction of diethyl phosphite sodium salt with the formed diethyl chlorophosphate.

In summary, this reaction is the new region of tellurium tetrachloride chemistry in that tellurium tetrachloride can be used as chlorinating agent for phosphorus nucleophiles such as di- or trialkyl phosphites.

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6. The product was identified by ^1H NMR, IR, Mass Spectra. $(EtO)_2P(O)Cl$: ^1H NMR ($CDCl_3$) d 1.41 (t, 6H), 4.28 (dq, 4H); Mass m/z (relative intensity, %) 147, 145 (M^+- C_2H_4, 10, 29), 119(100), 117(21).
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