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Dianisyltellurium (IV) Dichloride Promoted Oxidation Reactions of Di- and Triorganyl Phosphites

Sapana Garg, Rimpi and Verma KK*

Department of Chemistry, M. D. University, Rohtak-124001, India

ABSTRACT

Oxidation reactions of di- and triorganyl phosphites were carried out by using bis (*p*-anisyl) tellurium (IV) dichloride in carbon tetrachloride at ambient temperature. The di- and triorganyl phosphites were oxidized smoothly to afford the corresponding dialkyl/aryl chlorophosphates in considerable yield. The reaction probably proceeds by the attack of phosphorus centre of trivalent alkyl/aryl phosphite on the positive chlorine of $[\text{Ar}_2\text{TeCl}]^{\delta+} \text{Cl}^{\delta-}$ which is partially ionized form of dianisyltellurium(IV) dichloride in solution. During this reaction metallic tellurium is precipitated. All the products have been identified by comparison of their physical properties (boiling point, spectral studies) with those of authentic samples.

Keywords: Bis(*p*-anisyl)tellurium(IV) Dichloride, Diorganyl Phosphites, Triorganyl Phosphites Diorganyl Chlorophosphates

*Corresponding author



INTRODUCTION

As part of a programme aimed at developing organic synthetic method based on various organic derivatives of tellurium [1], we have found an efficient action of An_2TeCl_2 on the oxidation of di- and triorganyl phosphites using carbon tetrachloride as a solvent in nitrogen atmosphere giving rise to corresponding diorganyl chlorophosphate. During this reaction metallic tellurium is precipitated. The phenomenon means that oxidation reduction occurred in the reaction.

Though the Lewis acid character of Ar_2TeCl_2 has been recently utilized in the synthetic reactions [2, 3] including chlorotelluration [4], straight forward utilization of its oxidizing property has not been claimed so far in synthetic organic chemistry [5]. We were interested in the later property of Ar_2TeCl_2 and have now found a novel oxidative chlorination reaction which involves the oxidation-reduction reaction of a di- or triorganyl phosphite with Ar_2TeCl_2 . Mukaiyama and co-workers [6] reported a similar type of the reaction where trivalent phosphorus compounds were reacted with Hg (II) or Hg (I) resulting in the formation of P (V) and Hg (0). KOH and OH [7] reported similar reaction of diorganyl or triorganyl phosphites with TeCl_4 as a preparative method for diorganyl chlorophosphates.

MATERIALS AND METHODS

The ^1H NMR spectra were recorded in CDCl_3 on a Bruker AVANCE II Spectrometer operating at 400 MHz using TMS as internal standard. Infrared spectra were recorded in KBr pellets using a Bruker Tensor-27 FT-IR spectrophotometer. TLC plates of silica gel-G were used to monitor the reactions. All the products are known compounds and were characterized by IR, ^1H NMR spectral studies and identified by comparison of their properties with those of authentic samples.

Synthesis of bis(p-anisyl)tellurium(IV) dichloride [8]

Anisole (64.8 g, 0.6 mol) and TeCl_4 (27.0 g, 0.1 mol) were heated at 160°C for 6 h. The mixture was allowed to crystallize under vacuum to yield 30.6 g of bis (p-anisyl)tellurium(IV) dichloride. The product was recrystallized from acetonitrile as colourless crystals. M.pt $175\text{-}178^\circ\text{C}$, (lit m.pt $181\text{-}182^\circ\text{C}$) [8].

Typical experimental procedure for the oxidative chlorination reaction

To a solution of An_2TeCl_2 (0.227 g, 0.55 mmol) in 5 mL of carbon tetrachloride was added dropwise a solution of di- or triorganyl phosphite (1.0 mmol) in 5 mL of carbon tetrachloride under nitrogen atmosphere at $35\text{-}40^\circ\text{C}$. The reaction mixture was stirred for about 1 – 1.5 h. As reaction proceeded, the mixture became black due to precipitation of tellurium metal. The contents were then filtered and the filtrate was concentrated to give crude diorganyl chlorophosphate. The crude product was purified by silica gel column chromatography using EtOAc/n- hexane (1:2) as eluent in 72-85% yield. The results of reaction

with a variety of di- and triorganyl phosphites are listed in Table 1. The authenticity of the products was established by their spectral studies.

Dimethyl chlorophosphate (1), (b.pt 162-163 °C), ^1H NMR (400 MHz, CDCl_3) δ : 3.7465-3.7740 (d, 6H, CH_3). IR (KBr): 1270, 1050, 851 cm^{-1} .

Diethyl chlorophosphate (2), (b.pt 217 °C), ^1H NMR (400 MHz, CDCl_3) δ : 1.0015-1.0390 (t, 6H, CH_3), 3.7472-3.8207 (m, 4H, CH_2CH_3). IR (KBr): 1276, 1034, 822 cm^{-1} .

Di-n-propyl chlorophosphate (3), (b.pt 231 °C), ^1H NMR (400 MHz, CDCl_3) δ : 0.9771-1.0222 (t, 6H, CH_3), 1.6701-1.7588 (m, 4H, $\text{CH}_2\text{CH}_2\text{CH}_3$), 3.9668-4.0435 (q, 4H, $\text{CH}_2\text{CH}_2\text{CH}_3$). IR (KBr): 1271, 1011, 864 cm^{-1} .

Di-n-butyl chlorophosphate (4), (b.pt 279 °C), ^1H NMR (400 MHz, CDCl_3) δ : 0.9174-0.9544 (t, 6H, CH_3), 1.3734-1.4666 (m, 4H, $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 1.6309-1.7014 (quin., 4H, $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 4.0048-4.0552 (q, 4H, $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$). IR (KBr): 1231, 1031, 846 cm^{-1} .

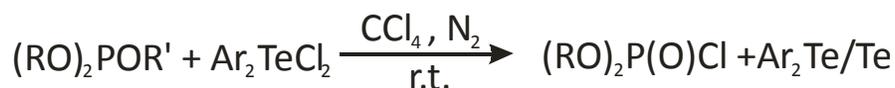
Di-iso-butyl chlorophosphate (5), (b.pt 270 °C), ^1H NMR (400 MHz, CDCl_3) δ : 0.5894-0.6391 (d, 12H, CH_3), 1.5852-1.6852 (m, 2H, $>\text{CH}-$), 3.4621-3.4946 (t, 4H, $-\text{CH}_2$). IR (KBr): 1280, 1046, 878 cm^{-1} .

Triphenyl chlorophosphate (6), (b.pt 314-316 °C), ^1H NMR (400 MHz, CDCl_3) δ : 7.1267-7.3140 (m, 10 H, ArH). IR (KBr): 1177, 951, 765 cm^{-1} .

Ditolyl chlorophosphate or di- o- cresyl chlorophosphate (7), (b.pt – 260 °C) ^1H NMR (400 MHz, CDCl_3) δ : 2.2697-2.2867 (d, 6H, $-\text{CH}_3$), 6.9538-7.2998 (m, 8H, ArH). IR (KBr): 1230, 1032, 735 cm^{-1}

RESULTS AND DISCUSSION

The oxidative chlorination of di- and triorganyl phosphites to yield the diorganyl chlorophosphate may be represented by Equation:



Usual aliphatic or aromatic di- and triorganyl phosphites are easily converted to corresponding diorganyl chlorophosphates in good yield. The reaction may proceed by the attack of phosphorus centre of trivalent organyl phosphite on the positive chlorine of $(\text{Ar}_2\text{TeCl})^{\delta+} \text{Cl}^{\delta-}$ which is the partially ionized form of Ar_2TeCl_2 in solution [9]. Initially formed Ar_2Te dissociates to Te which is precipitated out as black powder. The probable mechanism for the reaction is represented by Figure 1.

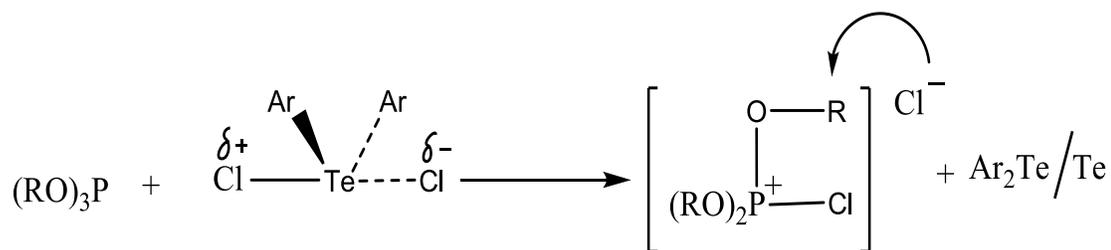


Figure 1: Mechanism of the Reaction

Table 1: Preparation of diorganyl chlorophosphates.

S. No.	(RO) ₂ POR		Time ^a (min.)	yield ^b (%)
	R	R'		
1	Me	Me	65	72
2	Et	Et	65	78
3	n-Pr	n-Pr	65	75
4	n-Bu	n-Bu	65	75
5	i-Bu	i-Bu	65	81
6	Ph	Ph	90	80
7	<i>o</i> -MePh	<i>o</i> -MePh	90	85
8	n-Bu	H	90	78

This reaction is the new region of dianisyltellurium(IV) dichloride chemistry in which dianisyltellurium(IV) dichloride can be used as an oxidizing and chlorinating agent for phosphorus nucleophiles such as di- or triorganyl phosphites.

CONCLUSION

The present chlorination is a novel type of redox reaction accompanying oxidation of P (III) to P (V) and reduction of Te (IV) to Te (II) / Te (0) and an alternative to the previously reported methods [6,7] for the formation of diorganyl chlorophosphates.

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