Phosphorus Tri-iodide (PI_3), a Powerful Deoxygenating Agent

By JEAN NOEL DENIS and ALAIN KRIEF*

(*Department of Chemistry, Facultes Universitaires N.D. de la Paix, 61, rue de Bruxelles, B5000 Namur, Belgium*)

Summary On reaction with PI_3 sulphoxides, selenoxides, aldehyde oximes, and primary nitroalkanes are transformed to sulphides, selenides, and nitriles, respectively.

RECENT results from our laboratory[1-3] show that phosphorus tri-iodide (PI_3), a readily available reagent,† is a powerful deoxygenator. We present here the preliminary results of our study concerning the reaction of PI_3 with sulphoxides (**1**, X = S), selenoxides (**1**, X = Se), aldehyde oximes (**3**), and nitroalkanes (**4**).

The PI_3-promoted reduction‡ of sulphoxides and selenoxides usually occurs readily even at very low temperatures, producing sulphides and selenides in high yield [equimolar amounts of PI_3, and oxide; CH_2Cl_2, −78 or 25 °C; equation (1); Table 1].

$$R^1X(:O)R^2 + PI_3 \xrightarrow{CH_2Cl_2} R^1XR^2 \qquad (1)$$

(**1**) (**2**)

TABLE 1.

X	R^1	R^2	T/°C	t/h	Yield of (**2**) (%)
S	Ph	Me	+25	0·1	83
S	Ph	Et	−78	0·2	91
S	Pr^n	Pr^n	−78	0·5	71
S	Ph	$CH{=}CHC_6H_{11}$	+25[a]	0·2	75
Se	Ph	$C_{10}H_{21}$	−78	1	93
Se	Ph	$C_6H_{13}CH(Me)-$	−78	1	95
Se	Me	$C_6H_{13}CH(Me)-$	−78	1	87

[a] At −78 °C this reaction does not occur at an appreciable rate.

Aldehyde oximes§ and terminal nitroalkanes¶ are transformed into nitriles simply by stirring at room temperature with 1 or 2 mol. equiv. of PI_3, respectively, in methylene chloride containing triethylamine [equations (2) and (3), Table 2]. Triethylamine is required for the success of the last reaction.

$$RCH{=}NOH + PI_3 \xrightarrow[NEt_3]{CH_2Cl_2} RC{\equiv}N \qquad (2)$$

(**3**) (**5**)

$$RCH_2{-}NO_2 + 2PI_3 \xrightarrow[NEt_3]{CH_2Cl_2} RC{\equiv}N \qquad (3)$$

(**4**) (**5**)

TABLE 2.

Starting material Compound	R	T/°C	t/h	Yield of (**5**) (%)
(**3**)	$C_{10}H_{21}$	25	0·25	85
(**3**)	$PhCH_2$	25	0·25	83
(**3**)	Ph	25	0·25	53[a]
(**4**)	C_9H_{19}	25	1	82

[a] I.r. spectroscopy indicates a trace of benzaldehyde.

The advantages of these transformations lie not only in the mildness of the conditions and in the high yields, but also in the ease of isolation of the desired products owing to the solubility in water of the phosphorus-containing by-products.

† From white phosphorus and iodine (1·3 mol) in CS_2.

‡ For other reagents which allow the same transformation see ref. 2 and references therein.

§ For other reagents which allow the same transformation see ref. 5. We also found that similar transformations to the one we describe can also be performed with 0·6 equiv. of P_2I_4 in the presence of triethylamine.

¶ For other reagents which allow the same transformation see refs. 2 and 6.

The mechanisms of some of the reactions remain uncertain and require more work. For instance a nitrile oxide as well as an oxime can be an intermediate in the nitroalkane–nitrile transformation. The reactivity of PI_3 towards other functional groups is being investigated, and we have found that 1,2-glycols are stereoselectively reduced to olefins (formal *syn* elimination), and that butyrolactone leads to γ-iodobutyric acid or methyl γ-iodobutyrate when the reaction is quenched with water or with methanol, suggesting the intermediary formation of a γ-iodo-acid iodide.

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