

Stereochemistry of Desulphurisation and Deoxygenation of Oxophosphoranesulphenyl Chlorides by Trivalent Phosphorus Compounds

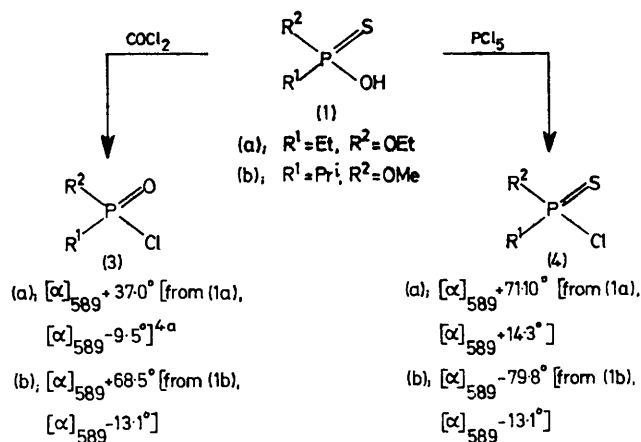
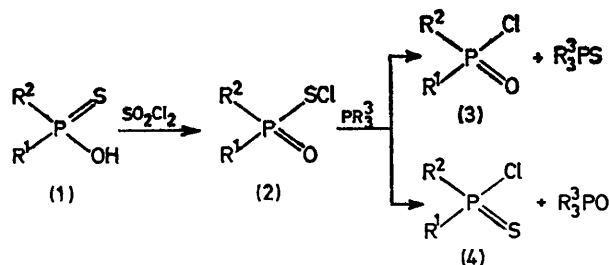
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Summary The ratio of desulphurisation to deoxygenation of oxophosphoranesulphenyl chlorides, $>P(O)SCI$, by trivalent phosphorus compounds depends on the nature of the P^{III} compounds and is accompanied by inversion of configuration at the chiral phosphorus atom of the sulphenyl chloride.

COMPOUNDS containing the $>P(O)SCI$ group, including those that are optically active, are readily accessible and exhibit pronounced chemical activity. Desulphurisation of oxophosphoranesulphenyl chlorides (2) by P^{III} compounds

purification to deoxygenation depends on the P^{III} compounds and also to some extent on the structure of the sulphenyl chlorides (Table). Mixtures of chlorides (3) and (4) were separated either by distillation or by crystallisation.



SCHEME

has been studied in this laboratory^{1,2} and we now report that deoxygenation can accompany desulphurisation and in many cases can even dominate it. The ratio of desul-

The reaction of (2a; $R^1 = Et, R^2 = OEt$), prepared from (1a; $R^1 = Et, R^2 = OEt$), $[\alpha]_{578} + 12.91^\circ$, with triphenyl-

TABLE. Deoxygenation and desulphurisation of the sulphenyl chlorides (2) by P^{III} compounds

Sulphenyl chloride		P ^{III} Compound	Deoxygenation	Desulphurisation	$[\alpha]_D$ of the mixture of (3) and (4)	$[\alpha]_D$ of (4)
R ¹	R ²		%	%		
EtO	EtO	(PhO) ₃ P	15	85		
		Ph ₃ P	90	10		
Et	EtO ^a	(PhO) ₃ P	10	90	-51.4°	+52.35°
		Ph ₃ P	40	60	-12.9°	+52.0°
Pr ^t	MeO ^b	(PhO) ₃ P	71	29	-29.2°	-62.8°
		Ph ₃ P	72	28	-36.3°	-65.3°
Bu ^t	Ph ^c	Ph ₃ P	100	0		-5.8 ^{cd}

^a From (1a), $[\alpha]_{589} +12.91^\circ$.
measured in benzene solution.

^b From (1b), $[\alpha]_{589} -9.76^\circ$.

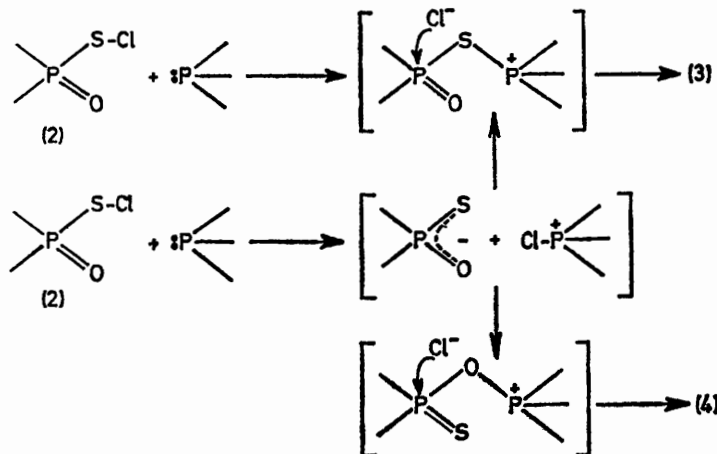
^c From (1c), $[\alpha]_{589} +17.50^\circ$ (EtOH).

^d The rotation value was

phosphine or triphenyl phosphite was carried out in benzene-ligroin solution at -5 to 0° . The chloride (4a) hydrolyses very slowly in comparison with (3a) and can be readily separated from the latter by mild alkaline hydrolysis. The proportions of (3a) and (4a) were determined by ³¹P n.m.r. spectra [(3a) $\delta -46.5$, (4a) $\delta -106.5$ p.p.m.]. The initial rotation values of reaction mixtures change dramatically

Relative configurations of the chlorides (3) and (4) have been determined by comparison with authentic samples prepared from optically active (1), by reactions of known stereochemistry, with phosphorus pentachloride³ and phosgene.⁴

It can be concluded that both desulphurisation and deoxygenation of (2) by P^{III} compounds proceed with



with time. In the reaction with triphenylphosphine the initial rotation value, $[\alpha]_{578} -12.9^\circ$ changed after 48 h to $[\alpha]_{578} +24.5^\circ$ and in the reaction with triphenyl phosphite from $[\alpha]_{578} -51.4^\circ$ to $[\alpha]_{578} +2.35^\circ$. In the latter case, the rotation after hydrolysis was $[\alpha]_{578} +52.0^\circ$, corresponding to a high optical purity of (+)-(4a). The rotational changes observed are in agreement with relatively fast racemisation of (3a) of rotation opposite in sign to (4a).

inversion of configuration at the chiral phosphorus atom. Consequently the conclusion of Ratajczak² that the reactions of (2) with triphenylphosphine and with triphenyl phosphite are of different stereochemistry needs correction.†

The mechanism suggested in the Scheme is in agreement with the observed stereochemical changes at the chiral phosphorus.

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† The results of Ratajczak are cited in recent reviews on phosphorus stereochemistry: J. Michalski, *Bull. Soc. chim. France*, 1967, 1109; M. J. Gallagher and J. D. Jenkins, 'Topics in Stereochemistry,' vol. 3, ed. N. L. Allinger and E. L. Eliel, Wiley, New York, 1968, p. 1; H. Christol and H. J. Cristau, *Ann. Chim.*, 1971, 6, 191.

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² A. Ratajczak, *Bull. Acad. polon. Sci., Sér. Sci. chim.*, 1964, 12, 145.

³ J. Michalski and M. Mikołajczyk, *Chem. and Ind.*, 1964, 661; J. Michalski and M. Mikołajczyk, *Tetrahedron*, 1966, 22, 3055; M. Mikołajczyk, J. Omelańczuk, and M. Para, *ibid.*, 1972, 28, 3855; J. Omelańczuk and M. Mikołajczyk, *ibid.*, 1971, 27, 5887.

⁴ (a) H. S. Aaron, A. T. Uyeda, H. F. Frack, and J. I. Miller, *J. Amer. Chem. Soc.*, 1967, 84, 620; (b) M. Mikołajczyk and J. Omelańczuk, unpublished results concerning the synthesis of (3b).