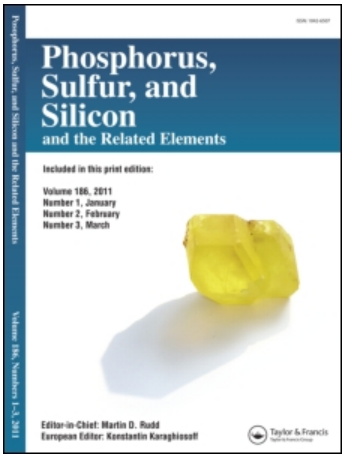

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THE ISOMERIZATION OF 3-PHOSPHOLENS IN DEUTERIOCHLOROFORM

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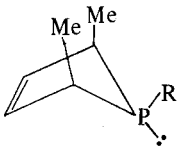
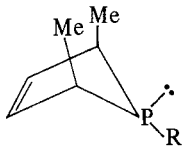
Cis-1-alkyl (or aryl)-2,5-dimethyl-3-phospholens isomerize to the *trans*-isomers in deuteriochloroform and the isomerization is probably due to small quantities of phosgene in the solvent.

It is well known that most phosphines are configurationally stable in solution at room temperature,[1] and this is especially true of cyclic phosphines such as the phosphetans and phospholans.[2] Consequently, the stereochemistry of many reactions at phosphorus has frequently been studied by employing diastereomers of heterocyclic compounds with phosphorus in four, five, six or seven-membered rings.[3-7] The conclusions of such studies are usually based on an appropriate stereochemical cycle and hence are secure, but in recent years considerable emphasis has been given to n.m.r. (particularly ^{1}H and ^{13}C n.m.r.) as a means of differentiating between diastereomers and assigning configuration at phosphorus.[1,8]

Separation of the diastereomeric 3-phospholens, **1a** and **2a**, was achieved by fractional distillation[9]

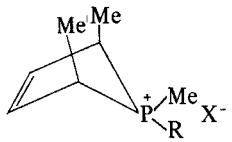


1a, R = Me
1b, R = Ph

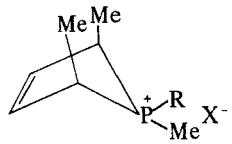


2a, R = Me
2b, R = Ph

using a Nester-Faust spinning band column. The ^{1}H, ^{13}C and ^{31}P n.m.r. data of both isomers are given in the Table. During the acquisition of this data we observed that in *deuteriochloroform*, **1a** was converted quantitatively to **2a** in less than 24 h using solvent from a freshly opened bottle of $CDCl_3$. However, the *cis*-phospholene, **1a**, is configurationally stable in CD_2Cl_2, CD_3CN or C_6D_6 and the implication is that either deuteriochloroform itself causes the isomerization or that some impurity in the solvent is responsible. The rate of isomerization in $CDCl_3$ was not altered by the presence of a small quantity (*ca.* 10%) of the



3a, R = H, X = Cl
3b, R = Cl, X = Cl
3c, R = $CH_2C_6H_5$, X = Br



4a, R = H, X = Cl
4b, R = Cl, X = Cl

phosphonium salt **3a** and the latter salt, precipitated from a benzene solution of **1a** by treatment with HCl gas, was configurationally stable in $CDCl_3$. Furthermore, **1a** in CD_2Cl_2, in the presence of a small quantity of **3a** was also configurationally stable. One may conclude that the isomerization is not due to trace amounts of HCl in the solvent, $CDCl_3$.

When, however, solutions of **1a** in CD_3CN, CD_2Cl_2 or $CDCl_3$ were doped with dilute solutions of phosgene in the same three solvents (so as to maintain an excess of **1a**) isomerization to **2a** occurred within five minutes of the addition of the phosgene solutions. Also, salt, **3b**, prepared by the addition of **1a** to an to an excess of phosgene in $CDCl_3$,[10] equilibrated to salt, **4b**, prepared from **2a** and excess phosgene, within thirty seconds of preparing the *cis*-salt.

Salt, **3c**, is easily prepared from **1a** and excess benzyl bromide in a stereospecific reaction (as demonstrated by n.m.r.) which presumably occurs with retention of configuration at phosphorus.[11] In the presence of **3c** in $CDCl_3$, **1a** isomerizes to **2a** within ten minutes. Furthermore, the presence of triphenylbenzyl phosphonium bromide, **5**, accelerates the rate of isomerization of **1a** to **2a** in $CDCl_3$ whereas **1a** is stable to salts, **3c** and **5** in CD_2Cl_2 or CD_3CN.

This provides clear evidence that bromide ion enhances the rate of isomerization presumably by exchange with labile chlorine in the solvent. This

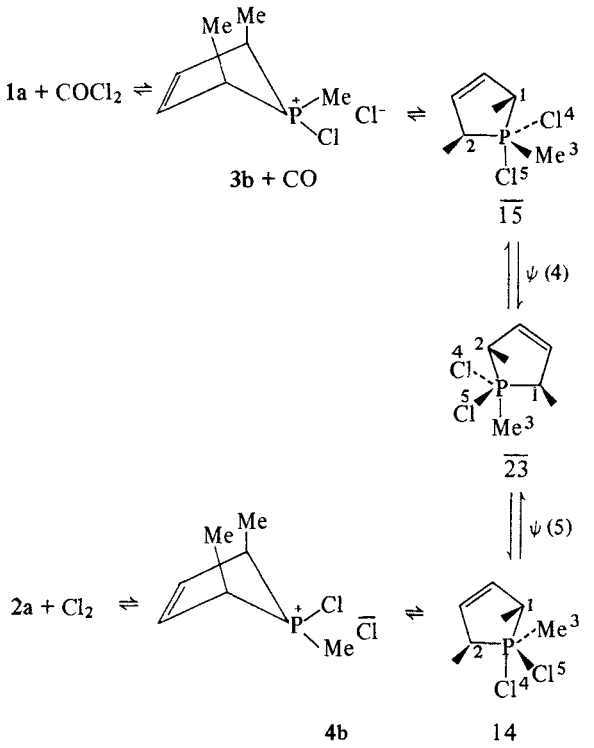
^{1}H, ^{13}C and ^{31}P n.m.r. data for 3-phospholens (in CD_2Cl_2)

Phospholen	δ ^{31}P (ppm, H_3PO_4)	^{1}H n.m.r. δ (ppm) TMS				^{1}H n.m.r. J_{P-H} (Hz)*				^{13}C n.m.r. δ (ppm) TMS				^{13}C n.m.r. J_{C-P} (Hz)			
		P–R	$C–CH_3$	=CH–	–CH–	P–R	$P–C–CH_3$	P–C–CH=	P–CH	P–R	C(2,5)	C(3,4)	$P–C–CH_3$	P–R	P–C(2,5)	P–C(3,4)	$P–C–CH_3$
1a (R = Me)	+ 6.0	0.75	1.12	5.55	2.85	3	10	6	~20[a]	0.5	38.2	134.5	13.9	24.4	12.2	4.9	0
2a (R = Me)	+ 7.1	0.97	1.19	5.65	2.35	3	17	6	~20[a]	12.8	43.4	134.1	21.0	18.6	9.8	3.7	28.1
1b (R = Ph)	−15.2	7.42	1.03	5.78	~3.1[b]	–	11	6	22	131.9[c]	40.2	131.9	14.7	–	12.3	d	0
2b (R = Ph)	−11.4	7.42	1.34	5.74	~3.1[b]	–	18	8	22	131.9[c]	43.9	131.9	22.0	–	11.0	d	30.5

* J_{CH-CH_3} = 7–8 Hz and $J_{-CH-CH=}$ = 1–2 Hz for all four compounds.
[a] Multiplet, not analysed precisely.
[b] Centre of multiplet from 2.66 to 3.51 ppm.
[c] Approximate position of multiplet of phenyl and olefinic carbons.
[d] Olefinic carbons indistinguishable from phenyl carbons.

conclusion was substantiated by the observation of an induction period of a few minutes in the presence of **5** in $CDCl_3$ prior to a rapid (<30 s) isomerization to **2a**. A similar series of observations has been recorded with **1b** although the isomerization process was slower.

The results strongly suggest that phosgene is responsible for the isomerization and a reasonable stereochemical pathway involving pseudorotation of pentaco-ordinate intermediates is shown in the Scheme.



Scheme to explain isomerization (**1a**) ⇌ (**2a**) *induced by* $COCl_2$

This scheme involves $\overline{23}$ as the high-energy intermediate, the alternative pseudorotation pathway being $\overline{15} \rightleftharpoons 24 \rightleftharpoons \overline{13} \rightleftharpoons \overline{25} \rightleftharpoons 14$ with $\overline{13}$ as the high energy intermediate.[12] As yet, there is no proof as to whether pseudorotation or nucleophilic attack of **1a** on $COCl_2$ constitutes the rate-determining step, but intuitively, since $COCl_2$ is a good electrophile,[10] one would anticipate the latter to be the case.[13] An alternative explanation not requiring pseudorotation of a pentaco-ordinate intermediate, would involve rate-determining nucleophilic (SN2P) displacement of Cl^- by Cl^- resulting in a direct conversion of **3b** to **4b**.

The implications of this work are considerable. In the first place, since synthetic routes to **1ab** and **2ab** generally produce an excess of the *cis*-isomers,[14] **1a** and **1b**, and these are more readily separable as pure diastereomers, one has a convenient route to both, pure diastereomers. Secondly, it seems reasonable to assume that other cyclic phosphines (phosphetans, phospholans, phosphorinans, phosphepans and phosphocans) may also be subject to isomerization in $CDCl_3$ and this is currently under investigation. Finally, where n.m.r. data are used to assign the configuration of cyclic phosphines one should obviously be cautious in the use of deuteriochloroform as solvent. We thank the S.R.C. for a grant (to P.J.H.).

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10. Probable structure based on nmr evidence and the work of R. Appel, B. Blaser and G. Siegmund, *Z. Anorg. Allgem. Chem.* 363, 177 (1968).
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12. Pathways involving pseudorotamers 34, 35 or 45 have been ignored since they would require the phospholene ring to be diequatorial. This is not necessarily legitimate, see for instance, D. B. Denney, *et al.*, *Phosphorus* **3**, 205 (1974).
13. This is backed by the observation that Br^- accelerates the rate (2 x Br equatorial in $\overline{23}$ or $\overline{13}$) and by the fact that isomerization of **1b** is slower than **1a**, since Ph and Me would be apical in $\overline{23}$ and $\overline{13}$ and Ph is less apicophilic than Me, see S. Trippett, *Phosphorus and Sulfur* **1**, 89 (1976).
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