Tetrahedron Letters, Vol.31, No.37, pp 5361-5364, 1990
Printed in Great Britain

0040-4039/90 $3.00 + .00
Pergamon Press plc

A SIMPLE SYNTHESIS OF DIMERIC 2,2-DISUBSTITUTED 1,3,2-BENZOXAZAPHOSPHOLES FROM PHOSPHORYL P^{IV}-COMPOUNDS.

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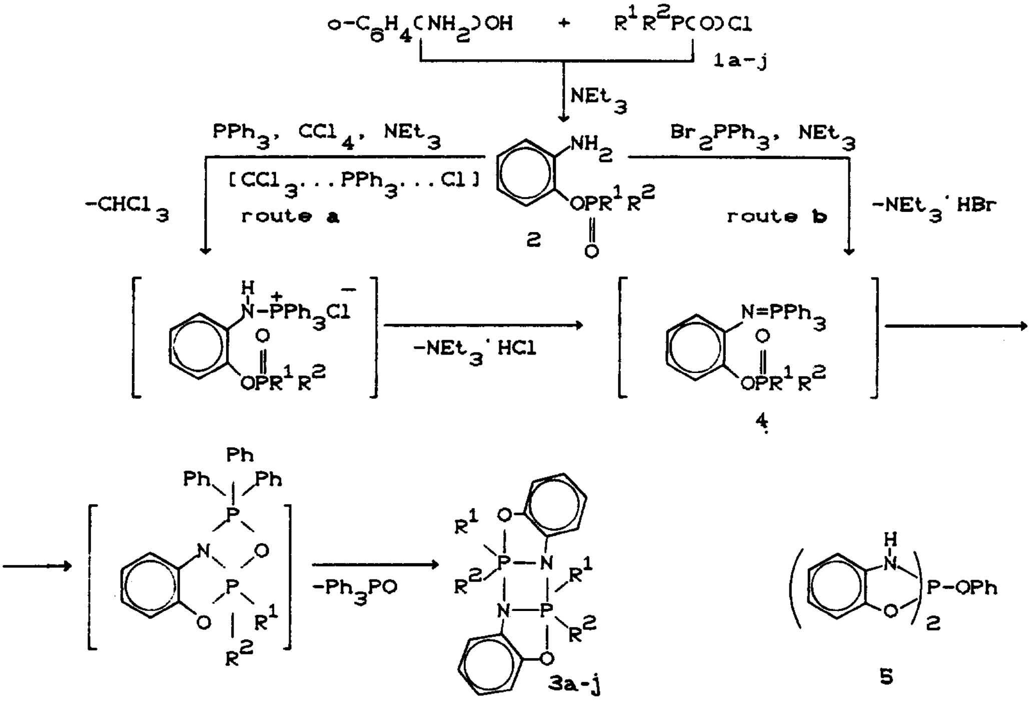
Dimeric 2,2-disubstituted 1,3,2-benzoxazaphospholes were prepared from o-aminophenyl phosphinates, phosphonates or phosphate by dehydration with PPh_3/CCl_4- or Ph_3PBr_2-reagents.

The title compounds usually are prepared from the substances of 3- or 5- coordinated phosphorus[1-3], but not from phosphoryl P^{IV}-compounds. We discovered that reaction of o-aminophenol with diphenylphosphinoylchloride (1a), particularly during the quick mixing of reagents, led not only to o-aminophenyl diphenylphosphinate (2a, 57%) but also to its dehydration product - dimeric 2,2-diphenyl-1,3,2-benzoxazaphosphole (3a, <10%)[4].

In search of the effective method of dehydration of the ester 2a, we found that PPh_3/CCl_4-reagent[5] easily converted the compound 2a to the dimer 3a in 85% yield under refluxing with NEt_3 in THF, dioxane, $CHCl_3$ or their mixtures. In this case the preparation of dimer 3a from o-aminophenol may be realized as an one-pot procedure without isolation of the intermediate ester 2a. By this way (route **a**) dimers 3b-i also were prepared[6] (table 1). The overall yield for the conversion of 1 to 3 by route a ranged from 51 to 85% (usually after a column chromatography). Supposing the reaction proceeded via the intermediate phosphazene compound 4, we attempted to prepare it directly by reaction of the ester 2a with Ph_3PBr_2 (route **b**), but it was found that after mixing of reagents at 20°C the precipitate of 3a began to appear a half hour later[7]. The compound 3j (table 1) was prepared by route **a** in 20% yield. In this case at first stage (1j→2j) a stable 2-phenoxy-2λ^5-2,2'(3H,3'H)- spirobi [1,3,2-benzoxazaphosphole] (5)[8] (m.p. 205-206°C) also was obtained in 20-25% yield. It is possible that the compound identified[1] as a dimer 3j (m.p. 201-202°C) and isolated from the reaction of o-aminophenol with PCl_5 followed by the treatment with phenol is a spirophosphorane 5.

The dimers 3e,f,h,i ($R^1 \neq R^2$) were prepared as a mixture of two



diastereomers (soluble and insoluble). Individual insoluble isomers 3e,f were isolated immediately after reaction, and others - by crystallization. The soluble isomer 3f was isolated as a benzene 1:2- and dioxane 1:1-complexes. They are converted into each other after recrystallization from the corresponding solvent and desolvated under vacuum drying at 110°C. X-Ray analysis[9] of the 1:2-complex demonstrated that more soluble isomer of 3f possess a cis orientation of chloromethyl or phenyl groups relative to the diazadiphosphetidine cycle (see figure 1).

The soluble isomer of 3e is assigned to have cis-configuration as it was based on comparison of ^{31}P NMR data of the dimers 3e,f, and hence the insoluble isomers of 3e,f have trans-configuration.

During the heating in the inert solvent (C_6H_6, $CHCl_3$, $C_6H_5NO_2$) the diastereoisomers converted into equilibrium mixture of cis- and trans-dimers as was shown by ^{31}P NMR spectroscopy (see table 1). For example isomers of 3e,h,i isomerized at 100°C in less than 3 h whereas the individual isomers of 3f converted into equilibrium mixture under warming to 120° within 2-3 h. The reaction between the two different dimers proceeded as easily as isomerization of the diastereomers[10]. The mixed dimers with two different atoms P were observed in ^{31}P NMR spectra as a

Table 1. Selective data for dimers 3a-j prepared by route a.

Compd	R^1, R^2	Total yield, %	M. p. °C(solvent) of soluble and insoluble isomers	$^{31}P\{H\}$, ppm[a] (nitrobenzene)
3a	Ph_2	85	226-227[b] dec.	-50.97 [c]
3b	Et_2	72	157-160[d](toluene)	-34.60
3c	Bu_2	61	120-124 (hexane)	-37.04[e]
3d	$(CH_2Cl)_2$	50	213-217 dec.(dioxane)	-48.89
3e	Me, Ph	57	149-151[f](dioxane); 178-182	-49.02, -47.98(3:2)
3f	CH_2Cl, Ph	80	177-182[g] (benzene); 186-189	-54.52, -53.97(4:1)
3g	$o-(CH_2O)_2C_6H_4$	63	225-230 dec.	-42.35
3h	CH_2Cl, OPh	51	141-143[f] (benzene); 146-149 (benzene)	-49.91, -49.34(2:1)[e]
3i	Ph, OPh	81	156-158 (benzene); 156-157	-53.63, -49.68(5:1)[e]
3j	$(OPh)_2$	20	174-176[h] (diethyl ether - benzene)	-62.29

a).Downfield signals (10-45 ppm) of possible monomers are not indicated. In brackets there is an equilibrium ratio of the soluble and insoluble isomers. b).210-220[3]. c).In all cases signal -41,62 ppm also was observed. d).169-170[1]. e).C_6D_6. f).Impured by the insoluble isomer. g).After a vacuum drying at 140°C. h).201-202[1] (perhaps spirophosphorane 5).

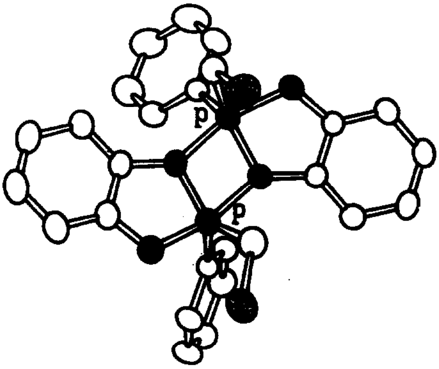


Figure 1. Molecular structure of soluble isomer 3f. The hydrogen atoms are omitted for clarity.

pair of dublets for which $^{2}J_{PP}$ varied from 22 Hz (mixed dimer from 3b and 3d) to 104 Hz (mixed dimer from 3i and 3j).

The dimers containing at least one diethylamino group at atom P were obtained by route **a** neither from $R(Et_2N)P(O)Cl$ ($R=Ph, CH_2Cl$) nor from corresponding o-aminophenyl esters.

Acknowledgements: We thank Ms A.N. Yarkevich for preparation of 1b and Dr. A.N. Pushin for the valuable advices.

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3. Cadogan J.I.G., Husband J.B., McNab H. J.Chem.Soc., Perkin Trans.I. 1984, 1449 and references therein.
4. Dimer 3a was prepared as insoluble residue after refluxing reagents in dioxane with triethylamine for 2 h.
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6. Typical procedure for preparing the dimers 3a-j. The chloroanhydride 1 (13 mmol) in THF (20 ml) was added to a stirring solution of o-aminophenol (13 mmol) and triethylamine (40 mmol) in dry dioxane or chloroform (30 ml) under argon atmosphere. After 30 min triphenylphosphine (16 mmol) and dry carbon tetrachloride (10 ml) were added and reaction mixture was refluxed with stirring for 1-1,5 h. Then additional amount of triphenylphosphine (up to 10 mmol) was added until dehydration of the intermediate ester 2 was completed by TLC monitoring. After cooling to 20°C and filtration of the precipitate the solvent was removed *in vacuo*, and the residue was chromatographed on silica gel (benzene) to afford dimers 3b-d,h-j and soluble isomers of 3e,f. In other cases the precipitate was washed by water and ethanol to afford the dimers 3a,g and the insoluble isomers of 3e,f. Analytically pure samples of dimers 3 were prepared not only by crystallization but also by their exposure in dry DMSO for 10 h with subsequent filtration and washing by ethanol. All compounds exhibited acceptable ^{1}H NMR spectra (when soluble) and mass-spectra as well as satisfactory elemental analysis data.
7. A solution of the ester 2a (10.0 g, 32 mmol) and triethylamine (6.0 g, 60 mmol) in dry chloroform (40 ml) was added to a stirred suspension of dibromotriphenylphosphorane (11,9 g, 28 mmol) in dry chloroform (50 ml). After stirring during 6 h at 20°C the precipitate was collected, washed by ethanol (2x20 ml) and then was dried and refluxed in dry dioxane (50 ml) for 10 min. The insoluble precipitate was dried *in vacuo* to afford 6.1g (85%) of 3a.
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9. The soluble isomer 3f crystallizes with benzene in the triclinic system: $C_{26}H_{22}Cl_2N_2O_2P_2 \cdot 2C_6H_6$, M=683.56; a=9.873(3), b=12.695(3), c=14.203(2) Å, α=84.34(2), β=81.70(2), γ=79.74(2)°, V=1728.5(9) Å^3, Z=2, space group $P\bar{1}$. The final R=0.043 for 2682 observed reflections measured on a CAD-4 diffractometer (MoKα-radiation).
10. Both isomerization and reaction between the different dimers were carried out in the sealed NMR ampule.

(Received in UK 11 July 1990)