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Synthesis of New Cyclic Phosphate of Arylglyoxylonitrile Oxime and Their Diastereomers

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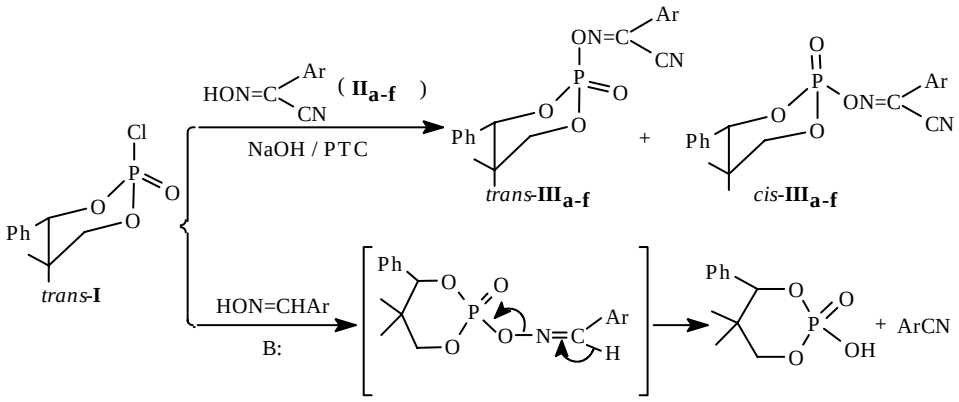
Abstract: Keeping in view the biological activities of 1,3,2-dioxaphosphorinane-2-one and oxime esters, some compounds possessing these two moieties have been synthesized. The configurational assignment and the ratio of *cis/trans* diastereomers of target products were performed on basis of ^{1}H NMR, ^{31}P NMR and confirmed by X-ray diffraction analysis.

Keywords: 1,3,2-Dioxaphosphorinane-2-one, arylglyoxylonitrile, diastereomers.

As part of our interest in the emergence of new compounds in the field of agrochemicals manufacturing, we have synthesized a series of structurally related compounds belonging to the two following families: 1,3,2-dioxaphosphorinane-2-one and oxime ester[1]. The cyclic phosphate introduced in our target molecule could serve as both a new carrier and an active part of the molecule.

Scheme-1.



Trans-2-chloro-2-oxo-4-phenyl-5,5-dimethyl-1,3,2-dioxaphosphorinane *trans*-**I** is easily obtained by refluxing a mixture of 1,3-propandiols and $POCl_3$ in dichloromethene[2]. The reaction of *trans*-**I** with arylglyoxlonitrile oximes $\mathbf{II_{a\text{-}f}}$ in the presence of phase transfer catalysts resulted in randomization of configuration on the phosphorus center,

giving both *trans*-**III$_{a-f}$** and *cis*-**III$_{a-f}$** (**Scheme-1**). The reaction of arylaldoxime with trans-**I** yielded unstable arylaldoxime cyclic phosphate which tends to decompose through Beckmann fragmentation to give the corresponding nitriles and cyclic phosphoric acid[3].

The configurational assignment and the ratio of *cis/trans* isomers of target products were performed on the basis of ^{1}H NMR, ^{31}P NMR. The 4-protons in axial position of *cis* isomers were expected to appear downfield owing to the deshielding by P=O. The *trans* isomers presented ^{31}P NMR chemical shifts at higher field than that of *cis* isomer because of the spectral electronic effect referring to the literature[4]. The reaction results are listed in **Table 1**.

Table 1. Stereochemistry Results of the PTC* Catalyzed Synthesis of **III$_{a-f}$**

ENTRY	Ar	^{1}HNMR(δ,ppm) *cis/trans*	^{31}PNMR(δ,ppm) *cis/trans*	yield(%) *(cis+trans)*	ratio *(cis:trans)*
III$_a$	Ph	5.65/5.36	-5.59/-9.96	96	1:10.64
III$_b$	o-Cl-Ph	~/5.42	~/-9.69	90	1:99
III$_c$	p-Cl-Ph	~/5.34	~/-9.56	91	1:99
III$_d$	p-t-Bu-Ph	5.58/5.35	-5.94/-10.09	95	1:4.35
III$_e$	p-OCH_3-Ph	5.52/5.33	~/-9.29	92	1:17.43
III$_f$	3,4-OCH_2O-Ph	5.53/5.32	~/-9.57	72.2	1:9.13

*PTC=$PhCH_2N(C_2H_5)_3Cl$

The spatial structure of *trans*-**III$_a$** has been confirmed by X-ray diffraction analysis[5]. It is shown that 4-phenyl is *trans* to the oxime moiety and the configuration of oxime moiety is Z.

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References and notes

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5 Crystallographic parameters have been deposited in the editorial office of CCL.

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