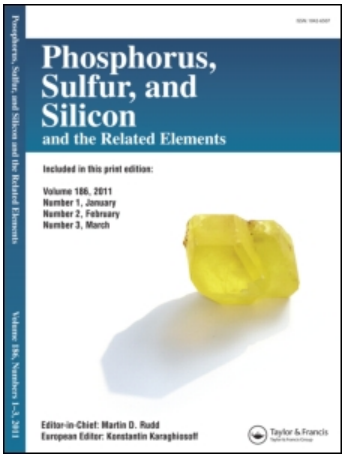

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Cyclic Oligophosphonic Anhydrides in Phosphonation of Diacylamides

Ivan S. Alferiev[a]
[a] Department of Pediatrics, University of Pennsylvania, School of Medicine, Philadelphia, Pennsylvania, USA

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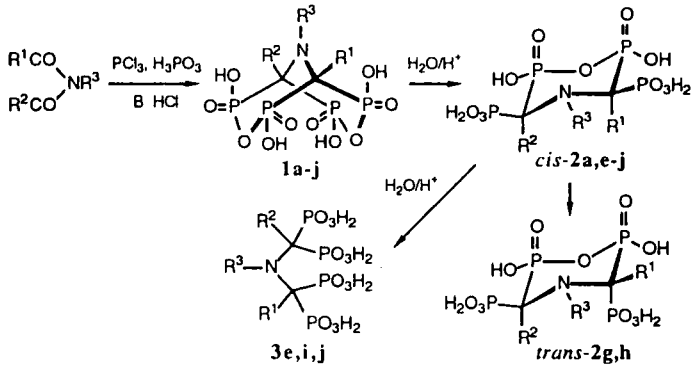
Cyclic Oligophosphonic Anhydrides in Phosphonation of Diacylamides

IVAN S. ALFERIEV

Department of Pediatrics, University of Pennsylvania, School of Medicine, Philadelphia, Pennsylvania 19104, USA

Diacylamides (10 compounds) were reacted with the system H_3PO_3 - PCl_3 in the media of amine hydrochlorides (conditions as in [1], B = Py, Bu_3N) and formed bicyclic dianhydrides **1** in high yields. The reaction failed when none of R was H and when R^1 and R^2 were a part of cycle. Less sterically hindered **1** were opened to monocyclic anhydrides **2** and to acyclic acids **3** using mild acidic hydrolysis.



a: R^1=R^2=Me, R^3=H; **b:** R^1=R^2=C_7H_{11}, R^3=H; **c:** R^1=Me, R^2=p-$CH_3C_6H_4$, R^3=H; **d:** R^1=Me, R^2=$C_{11}H_{23}$, R^3=H; **e:** R^1=Me, R^2=R^3=H; **f:** R^1=p-$CH_3C_6H_4$, R^2=R^3=H; **g:** R^1=Me, R^2=H, R^3=Me; **h:** R^1=C_9H_{19}, R^2=H, R^3=Me; **i:** R^1=R^2=H, R^3=Me; **j:** R^1=R^2=H, R^3=$C_{14}H_{29}$

As a rule, only one of the two possible diastereomers of **2** formed in the hydrolysis (probably having the *cis*-structure). In two cases *cis*-isomers (**2g,h**) were labile, and transformed into the stable *trans*-**2g,h** under the conditions of hydrolysis. The compounds **1b,c**, **2a,e,f** (most likely - *cis*-isomers), *trans*-**2g,h**, *cis*-**2h** and **3e,i,j** were isolated from the reaction mixtures as pyridine or aniline salts. In addition to ^{31}P NMR, the structures of isolated compounds were demonstrated by ^1H NMR and elemental analysis. Both **1** and **2** are stable in alkaline and neutral media. Most of **1**, **2** and **3** decompose in hot acidic aqueous solutions with elimination of a half of phosphorus in the form of H_3PO_3.

References

[1] I.S. Alferiev and S.Yu. Bobkov, *Z. Naturforsch.*, **47b**, 1213 (1992).