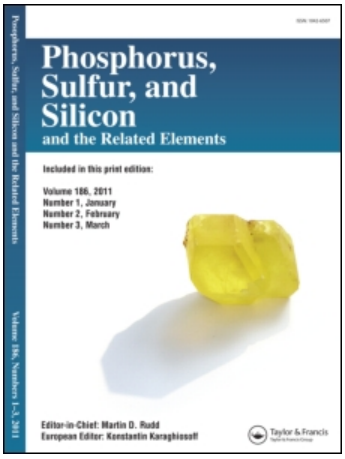


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# Novel One-pot Syntheses for Oligo-phosphonic and Phosphinic-Acid Esters

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# NOVEL ONE-POT SYNTHESES FOR OLIGO-PHOSPHONIC AND PHOSPHINIC-ACID ESTERS

G. HÄGELE, U. FISCHER, A. GAEDCKE, H. RIDDER, A. SINKIEWICZ, E. WILKE AND J. SEEGA

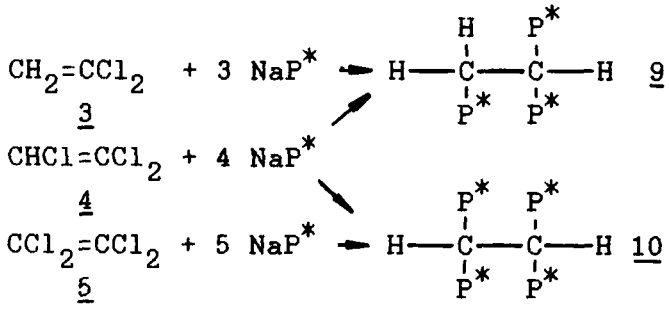
Abstract Sodium salts of phosphorous acid dialkyl esters or alkane phosphonous acid monoalkylesters react with chlorinated olefines and acetylenes to form tris- and tetrakis-phosphonic or phosphinic acid esters in good yields. Corresponding acids are obtained from esters by cleavage with HCl. Reaction mechanisms and molecular structures are investigated by 1D and 2D NMR studies.

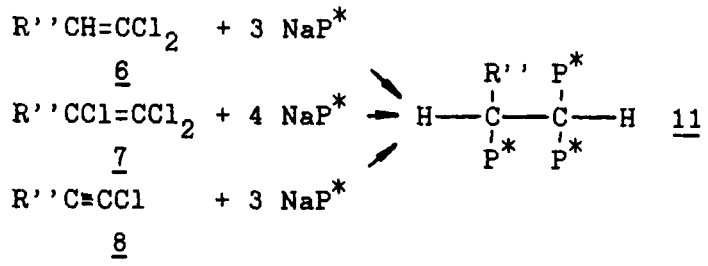


Sodium salts of type 1 and 2 react with chlorinated olefines and acetylenes 3 - 8 to yield substituted ethane tris- and tetrakis phosphonic or phosphinic acid esters 9 - 11:

$NaP^* = Na\text{-}O\text{-}P(OR)_2$, $Na\text{-}O\text{-}P(R')OR$

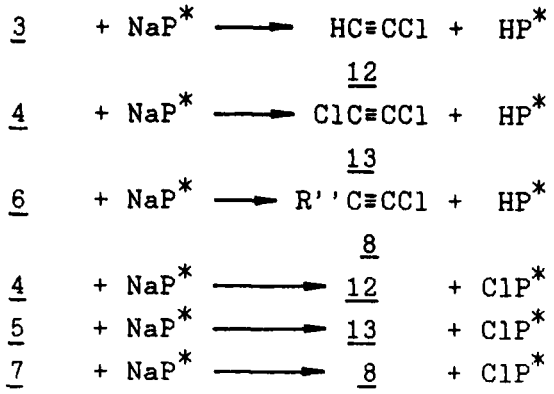
1 2



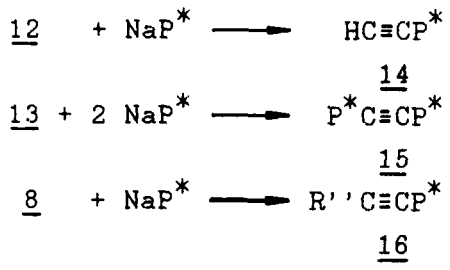


R = Et, iPr, iOc, iBu; R' = Me; R'' = Ph, tBu;
$P^*$ = $P(O)(OR)_2$, R'P(O)OR

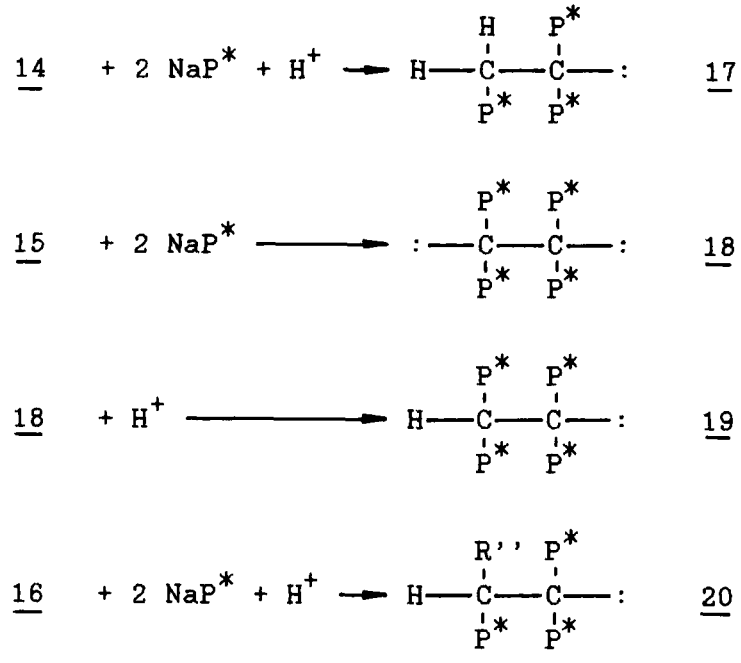
Chloroacetylenes 12 - 14 are formed as intermediates via abstraction of H/Cl or Cl/Cl units:



Phosphorylated acetylenes 14 - 16 are formed via Michaelis-Becker-type-reactions:

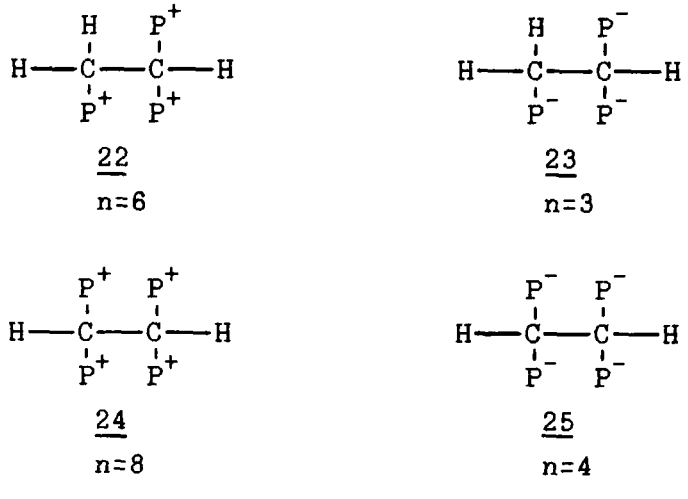


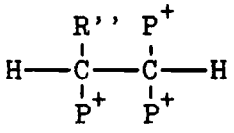
Pudovik-type-additions lead to carbanions 17 - 20:



which upon re-protonation lead to the corresponding neutral esters 9 - 11.

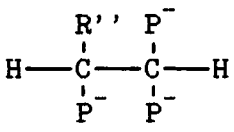
Acidolysis of 9 - 11 with conc. HCl or HAc leads to corresponding oligo phosphonic or phosphinic acids 21 - 27, which are 3 - 8 basic acids in protolytic equilibria:





26

n=6



27

n=3

$P^+ = P(O)(OH)_2$; $P^- = R'P(O)OH$

Titrations with $KOH/D_2O$ in combination with proton decoupled P-31 NMR spectroscopy at 81 MHz were performed. Dissociation and complex formation are combined with intramolecular rotation of phosphonic and phosphinic acids, strongly influencing the NMR parameters of corresponding solutions. Addition of 18-crown-6 deduced interactions between phosphonate ligands and potassium ions.

Particular attention was paid towards 2D NMR studies. H,H-COSY spectroscopy was used to explain non-equivalence phenomena in prochiral ester units of oligo phosphonic acids.

P,P-COSY technique discovered two individual rotameric forms stable separately at least up to 150°C for a compound of type 11 ($P^* = P(O)(OEt)_2$; R'' = tBu).

Esters 9 - 11 of oligo phosphinic acids ($P^* = CH_3P(O)OiBu$) have 3 and 4 P-chiral centers respectiveley, giving rise to mixtures of P-epimers, which were investigated by means of P,P-COSY spectroscopy.