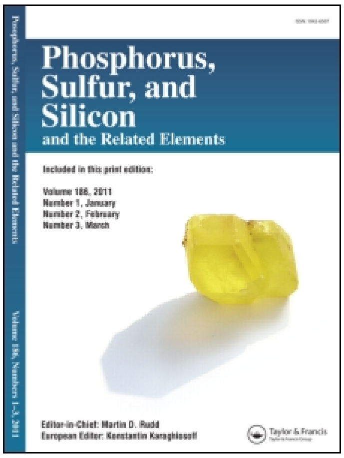

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Salts of α-Diazo "Phosphorus Acids" - Starting Compounds for Phosphonate and Phosphate Transfer Reagents

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To cite this Article Regitz, Manfred and Martin, Roland(1983) 'Salts of α-Diazo "Phosphorus Acids" - Starting Compounds for Phosphonate and Phosphate Transfer Reagents', Phosphorus, Sulfur, and Silicon and the Related Elements, 18: 1, 163 — 166

To link to this Article: DOI: 10.1080/03086648308075992

URL: http://dx.doi.org/10.1080/03086648308075992

Phosphorus and Sulfur, 1983, Vol. 18 pp. 163-166
0308-664X/83/1801-0163/$18.50/0

SALTS OF α-DIAZO "PHOSPHORUS ACIDS" - STARTING COMPOUNDS FOR PHOSPHONATE AND PHOSPHATE TRANSFER REAGENTS

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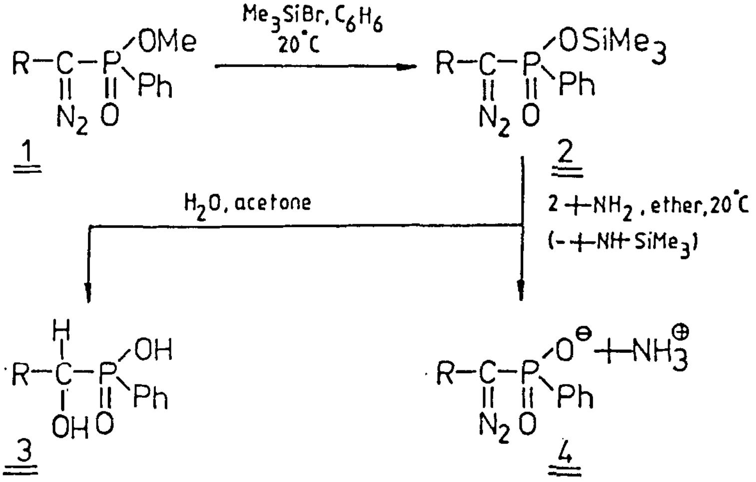
Abstract Pyrazoles bearing N-phosphonate and phosphate groups are well accessible from salts of α-diazo "phosphorus acids" and electron poor acetylenes. They are good phosphorylating reagents for protic nucleophiles.

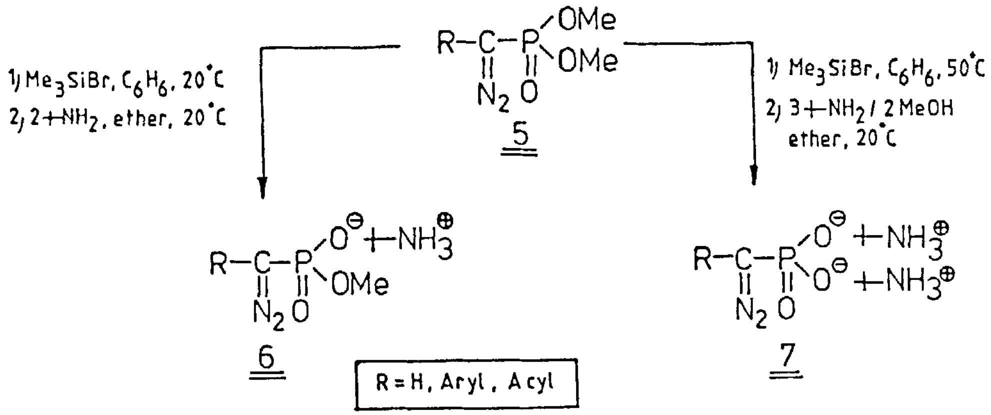
The α-diazophosphinates 1 - well accessible by diazo group transfer or by electrophilic diazoalkane substitution - are transformed into the trimethylsilylesters 2 without destruction of the diazo group by treatment with bromo trimethylsilane [1]. They are extremely sensitive against water and decompose under desilylation and N_2-loss to form the α-hydroxyphosphinic acids 3.



4: R=H, Alkyl, Aryl, Acyl, over all yield > 70%

In contrast to that and without attack of the diazo unit the silylesters 2 can be solvolysed with two equivalents of tert-butyl amine to yield the hitherto unknown ammonium α-diazophosphinates 4.

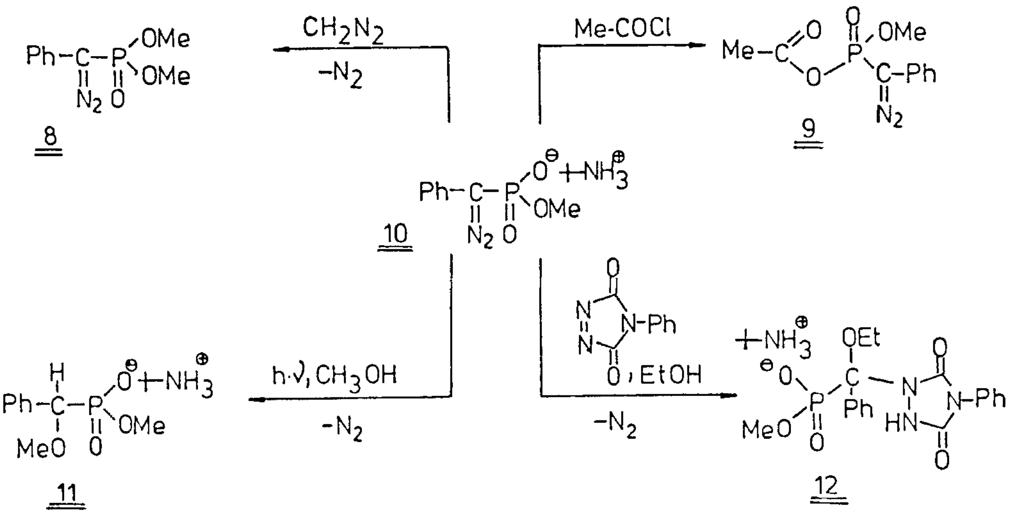
In an analogous way the α-diazophosphonates 5 react with bromo trimethylsilane followed by tert-butyl amine treatment either to the ammonium methyl α-diazophosphonates 6 or to the bis(ammonium) α-diazophosphonates 7 depending on the molar ratio of both reaction partners. The cleavage of the second methoxy group only takes place at elevated temperature.



The constitution of the new diazo compounds is based on the analytical data and on ir, ^{1}H-, ^{13}C- and ^{31}P n.m.r. evidence.

Chemical arguments for the constitution of the diazo salts examplarily are given for 10. Methylation with diazomethane to 8 and acylation with acetyl chloride leading to the mixed anhydride 9 leave the diazo group unattacked.

In contrast to that the photolysis of 10 in methanol such as the reaction with the strong electrophile 1-phenyl-1,3,4-triazoline-2,5-dione in the presence of ethanol proceeds under the loss of the diazo nitrogen (formation of 11 and 12).

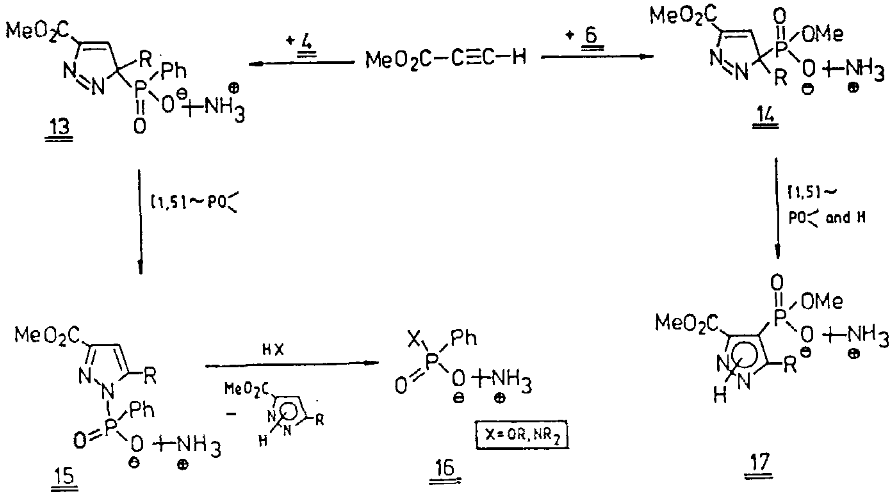


The transformation of the diazo salts **4** into phosphonate group transferring reagents is accomplished by [3+2] cycloaddition reaction with methyl propiolate, in the first step leading to the non isolable 3H-pyrazole **13**.

Subsequent [1,5]-sigmatropic phosphoryl group migration[2] produces the actual phosphorylating reagent **15**.

Protic nucleophiles HX like amines or alcohols are phosphorylated by **15** under smooth conditions (formation of the phosphonates **16**).

An analogous reaction sequence is unsuccessful for the production of the corresponding phosphate group transferring reagent: The cycloaddition reaction between the same acetylene and **6** leading to **14** is followed by a series of sigmatropic PO- and H-migrations, which in the last consequence afford the NH-pyrazole **17**.



Nevertheless the [3+2]-cycloaddition reaction with 6 and dimethyl acetylene dicarboxylate instead of methyl propiolate produces the true phosphorylating pyrazole (15: OMe instead of Ph and CO_2Me instead of CH-Pyrazole). Alcohols, amines and hydrazines are phosphorylated without complications to the corresponding phosphates; 2-aminoethanol is selectively phosphorylated at the more nucleophilic amino group.

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