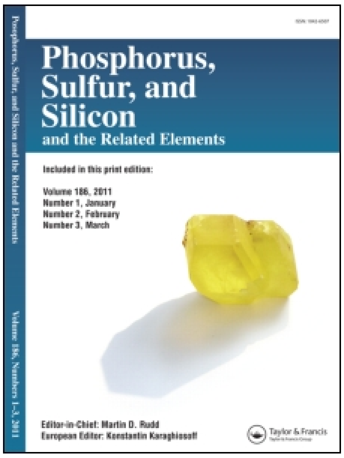

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Phospha-alkynes - Useful Building Blocks in Organic Chemistry[1]

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PHOSPHAALKYNES - USEFUL BUILDING BLOCKS IN ORGANIC CHEMISTRY [1]

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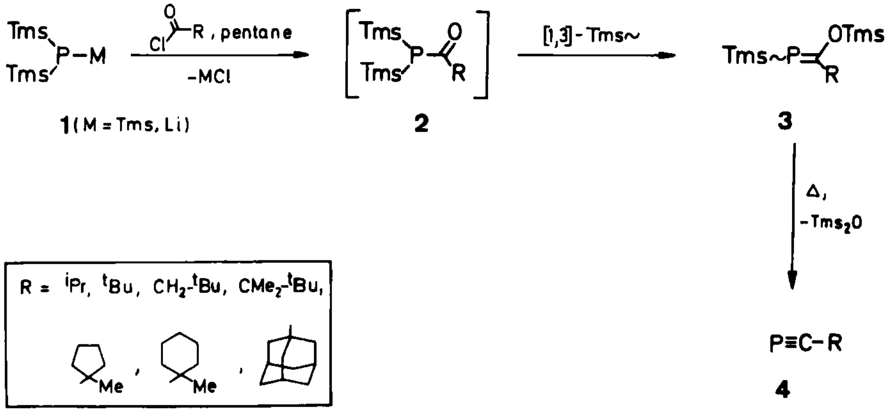
Abstract: The syntheses of phospholes (7, [3+2]-cycloaddition), bicyclophosphaalkenes (17, [4+2]-cycloaddition), and phosphabenzenes (15, [4+2]-cycloaddition followed by an extrusion process) starting from the phosphaalkynes (4) are described. The 2-Dewar phosphabenzene 18, obtained from the cyclobutadiene 21 and 4 (R = ^{t}Bu), is the starting material for the synthesis of the valency isomers 19, 20, 22, and 23.

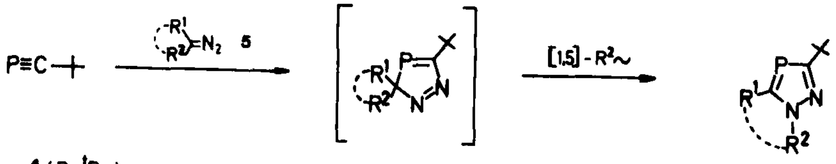
PHOSPHAALKYNES

A wide variety of phosphaalkynes are accessible through the reaction sequence 1 → 2 → 3 → 4[2,3,4]. The decisive hexamethyldisiloxane elimination step (3 → 4) can be performed with the best results by using solid sodium hydroxide at 110-160 °C.



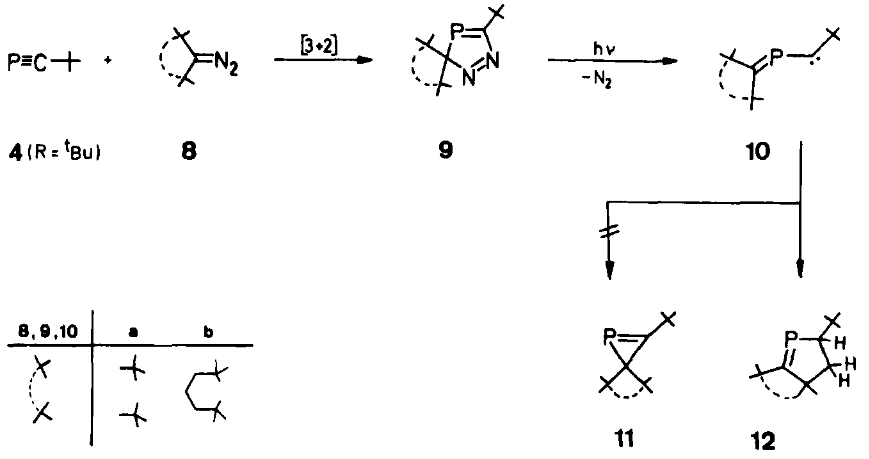
CYCLOADDITION REACTIONS

Even phosphaalkynes with sterically demanding substituents exhibit a pronounced tendency to take part in cycloaddition reactions. Thus, diazo compounds 5 (R^2 = H or acyl) undergo regiospecific [3+2]-cycloadditions with 4 (R = ^{t}Bu) to form the 3H-1,2,4-diazaphospholes (6) which spontaneously aromatize via [1,5]-H- or -acyl shifts to yield the compounds 7[5].



4 (R = ^{t}Bu) 6 7

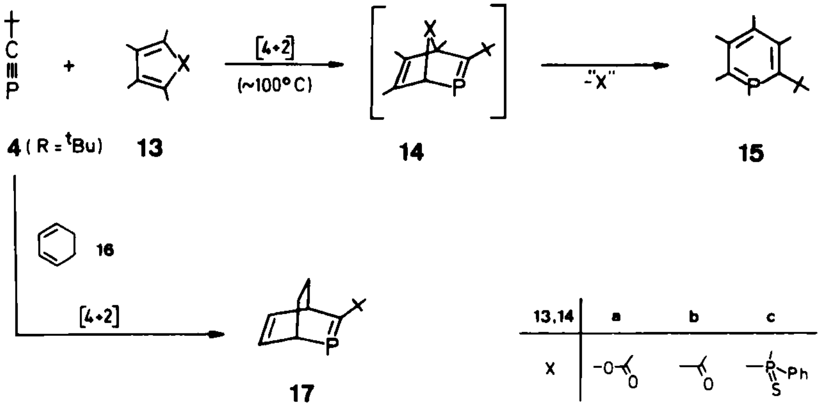
The primary products 9a and b can be isolated from the reactions of 8a and b with 4 (R = ^{t}Bu). Photolysis of these compounds generates carbenes of the type 10, which stabilize by C/H insertions to yield the phosphacyclopentenes 12a and b. The actually expected 1,3-ring closure to give the 1-phosphirines (10 → 11) is completely avoided.



4 (R = ^{t}Bu) 8 9 10 11 12

Other octet-stabilized 1,3-dipoles such as azides, nitrile oxides, nitrile sulfides, and nitrile imines as well as mesoionic compounds such as sydnones and münchnones also undergo addition to phosphaalkynes (the latter reactions are accompanied by cleavage of CO_2) and, thus, open an access to a wide variety of phospholes containing further heteroatoms.

Diels-Alder reactions of 4 (R = ^{t}Bu) with α-pyrones (13a), cyclopentadienones (13b), and phosphole sulfides (13c) result in the formation of the phosphabenzenes (15) in high yields; the bicyclic intermediates (14) cannot be detected directly as they undergo spontaneous aromatization with elimination of the X-bridge[6].

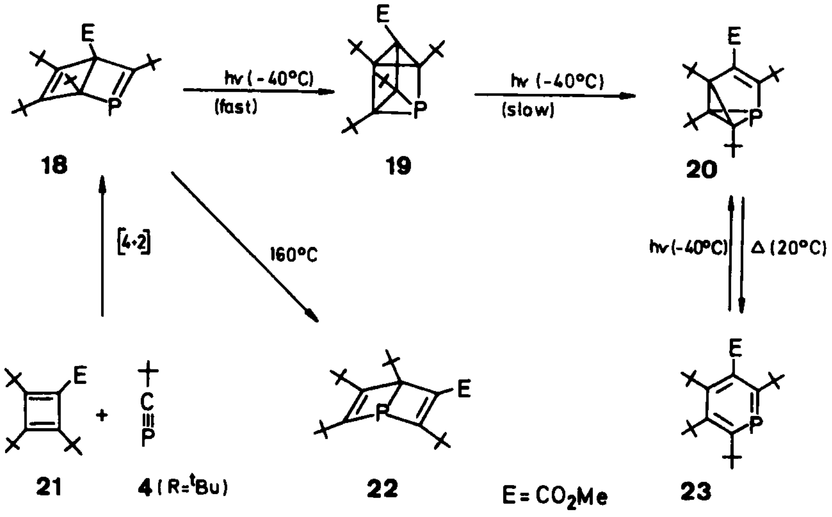


In contrast, bicyclic adducts of the type 17, obtained from the reactions of 4 (R = ^{t}Bu) with cyclohexadiene (16) (or anthracene), can be isolated without difficulty.

Phosphaacetylene itself, generated from dichloromethylphosphine at 1150 °C/10^{-5} torr, reacts analogously with 1,3-dipoles and 1,3-dienes.

PHOSPHABENZENE VALENCY ISOMERIZATION

The starting point for the synthesis of the previously unknown valency isomers of phosphabenzene is the reaction of the cyclobutadiene 21 with 4 (R = ^{t}Bu) which yields the 2-Dewar phosphabenzene 18[7]. Under thermal conditions this compound is transformed smoothly to the 1-isomer 22, whereas, under photochemical conditions, an intramolecular [2+2]-cycloaddition reaction to give the phosphaprismane 19 occurs.



Further photolysis of the tetracycle 19 gives an access to the phosphabenzvalene 20 which is in a thermal or photochemical, respectively, transformation relationship with the phosphabenzene 23.

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