Studies on the behavior of different phoshorus reagents toward active centers in certain organic compounds.

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g]chromen-7-ylidene)benzenamine (5b), and the second minorproduct was 4,9-dimethoxy-5-methyl-7H-furo[3,2-g]chromen-7-one(8b). Compound 8b was obtained by partial hydrolysis of 5b(Scheme 1).O O CH3ROCH3 O1a, R= Hb, R = OCH3KOHH2O OROCH3 COHCH3O2a, R= Hb, R = OCH3Ph3P C C N Ph3in THF, at room temp.OROCH3 COCH3O4a, R= Hb, R = OCH3CN PhHC PPh3 - Ph3P = OO O NROCH35a, R= Hb, R = OCH3CH3Ph+O O OOCH3OCH3CH3Scheme 18bThe reaction of (2-oxovinylidene)triphenylphosphorane (6) with 2aand 2b was also investigated, to give (triphenyl-acetic acid-5-acetyl-4-methoxy-benzofuran-6-ylester (7a) and(triphenyl-6-yl ester (7b), respectively. When the phosphoranes 7aand 7b are boiled in toluene, intramolecular Wittig reaction occurswith the formation of -4-methoxy-5-methyl-7H-furo[3,2-g]chromen-7-one (8a) and 4,9-dimethoxy-5-methyl-7H-furo[3,2-g]chromen-7-one(8b) respectively, together with TPPO. The reaction of the stabilizedphosphonium ylide carbmethoxymethylenetriphenylphosphorane (9)with compounds 2a and 2b, affords the chromenones 8a and 8brespectively. In this case the stabilized phosphonium ylide 9 reactswith the acetyl carbonyl group rather than the OH group to give theSummary of part 1IVintermediates 10a and 10b which are lactonized to give compounds8a and 8b with elimination of methanol (Scheme 2).Ph3P C C O6in THF, at room temp. OROCH3 COCH3O7a, R= Hb, R = OCH3COHC PPh3- Ph3P = OTolueneO O OROCH38a, R= Hb, R = OCH3CH3CHC OCH3OPh3P9in tolueneOROCH3 COHCH3CH10a, R= Hb, R = OCH3C OOCH3Scheme 22a,b-CH3OHIn addition the reaction of the phosphacumulenes 3 and 6 with 1-(6-hydroxy-4-methoxybenzofuran-5-yl)-3-phenylprop-2-en-1-one (11a)and 1-(6-hydroxy-4,7-dimethoxybenzofuran-5-yl)-3-phenylprop-2-en-1-one (11b) was studied, too. The corresponding chromenes 13a-dwere obtained together with TPPO. Formation of compounds 13a-dcan be explained by the addition of the phenolic OH group of 11a,bto the phosphacumulenes 3 and 6 to give first the phosphonium ylides12a-d which then cyclized to the chromenes 13a-d.The reaction of the oximes 14a and 14b with the phosphacumulenes 3and 6 was performed to give the isoxazoles 15a and 15b. In this case,cyclization occurred with the formation of the isoxazole ring and noreaction was observed between compounds 14a and 14b and thephosphorus reagents 3 and 6. In this senses the phosphacumuleneSummary of part 1Vylides 3 and 6 acts as Lewis bases that facilitate the dehydration process(Scheme 3).OROCH3 COHCH3O2a, R= Hb, R = OCH3benzaldehydeNaOHOROCH3 COHCO11a, R= Hb, R = OCH3C Ph Ph3P C C X3, X = N- Ph6, X = OOROCH3 COHCO12a-dCXHC PPh3HCPhO O XROCH3C C Ph13a, R = H; X = N- Phb, R = OCH3; X = N- Phc, R = H; X = Od, R = OCH3; X = ONH2OH, HClOROCH3 COHCH3NOH14a, R= Hb, R = OCH3Ph3P C C X3, X = N- Ph6, X = OOROCH315a, R= Hb, R = OCH3ONCH3Scheme 3H HH H+ Ph3P = OThe reaction of 7-hydroxy-5-methoxy-2-methyl-4-oxo-4H-chromene-6-carbaldehyde (16) with the phosphacumulenes 3 and 6 was alsoinvestigated. Compound 16 was prepared by oxidation of the chromenone1a with K2Cr2O7 and H2SO4. Treatment of the chromene carbaldehyde16 with the phosphoranes 3 or 6 leads to the formation of5-methoxy-2-methyl-8-phenylimino-8H-pyrano[3,2-g]chromen-4-one(18a) and 5-methoxy-8-methylpyrano[3,2-g]chromen-2,6-dione (18b)Summary of part 1VIrespectively, along with TPPO. Compounds 18a and 18b are formedthrough intramolecular cyclization of the intermediates 17.The reaction of 7-hydroxy-5-methoxy-2-methyl-6-[(phenylimino)-methyl] 4H-chromen-4-one (19) -with the phosphacumulene 3afforded the chromenone 18a together with N phenyliminotriphenylphosphorane(21). However when chromenone 19 was allowed to reactwith phosphacumulene 6, the ester 20b was exclusively -obtained.Cyclization of 20b afforded 5-methoxy-8-methyl pyrano[3,2-g]chromene-2,6-dione (18b) and the phosphinimine 21. It is evidentthat formation of compounds 18a and 18b involves the intermediates20a and 20b which is spontaneously lactonize only in case of 20a(Scheme 4).O O CH3OCH3 O1aK2Cr2O7H2SO4HO O CH3OCH3 O16HCOPh3P C C X3, X = NPh6, X = OO O CH3OCH3 O HCOCXPh3P CH17X O O CH3OCH O 318a, X = N- Phb, X = ONaOHaniline hydrochlorideHO O CH3OCH3 O19HCPh NPh3P C C X3, X = N- Ph6, X = OO O CH3OCH3 O HCNCXPh3P CH20a, X = N- Phb, X = OPhPh3P N PhScheme 421- Ph3P=O-+Summary of part 1VIIThe reaction of the phosphacumulenes 3 and 6 with 4-methoxy-5-oxo-5H-furo[3,2-g]chromene-6-carbaldehyde (22a) and 4,9-dimethoxy-5-oxo-5H-furo[3,2-g]chromene-6-carbaldehyde (22b) wasperformed. Compounds 2a and 2b are used for the synthesis of thecarbaldehydes 22a and 22b directly via Vielsmeier-Haack reaction.The reaction of the chromene carbaldehyde 22a with the phosphorane3, resulted in the formation of the cyclobutylidene 25a. While the reactionof compound 22b with 3 gave the cyclobutylidene 25b and thephosphanylidene-cyclobutylidene (26). This reaction proceeds via a[2+2]-cycloaddition of the carbonyl group in 22a and 22b to the ylidicC-P bond of the phosphorane 3 to give the oxaphosphetane 23.Elimination of TPPO from 23 leads to the formation of the unstableketene 24, which dimerizes to give 25a and 25b. However in case ofthe reaction of the chromene carbaldehyde 22b with the phosphorane3, the dimer 25b was isolated together with the cyclobutylidenechromenone 26, which is formed by addition of 3 to the ketene 24(Scheme 5).Summary of part 1VIIIOROCH3 COHCH3O2a, R= Hb, R = OCH3O OROCH3 O22a, R= Hb, R = OCH3CHO23O OROCH3 OCHO C C N PhPh3PO OROCH3 OHC C CO OROCH3 OCHPh NN PhCHOOROCH3O2425a, R = Hb, R = OCH3+O OOCH3OCH3 HCNPPh3NPhPh26Ph3P C C N Ph3POCl3DMFOScheme 5N Ph- Ph3P = OThe reactions of the carbaldehydes 22a and 22b with the phosphacumulene6 was performed and yield compounds 27a and 27brespectively (Scheme 6).O OROCH3

OCHOO27a, R = Hb, R = OCH3Ph3P C C O6Scheme 622a,bPPh3The structure of the new products was assigned according to consistentanalytical and spectroscopic data (IR, 1H-, 13C-, 31P- NMR andMS).