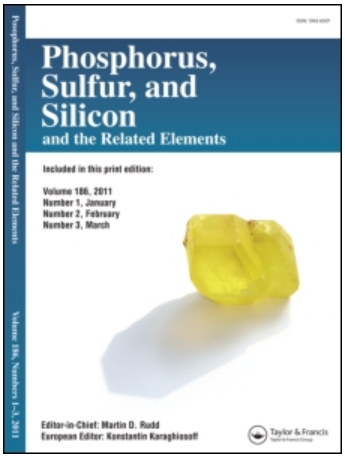

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Novel approaches to dialkylhetarylphosphonates

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NOVEL APPROACHES TO DIALKYLHETARYLPHOSPHONATES

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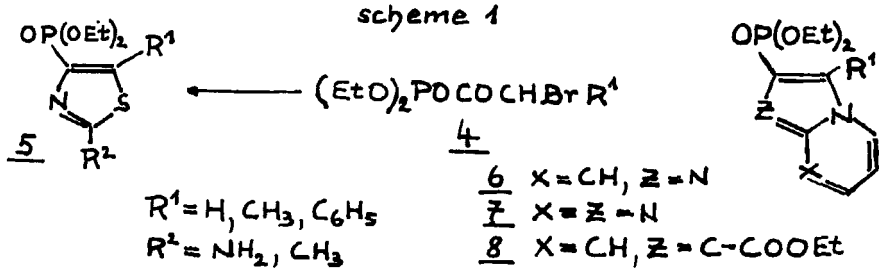
Abstract Dialkyl-1-oxoalkyl-, 1-oxo-2-alkenyl-, and 3-oxo-1-alkenylphosphonates are very useful substrates for the synthesis of a series of Dialkylphosphonates with a heterocyclic substituent.

Since the discovery of some interesting biologically active phosphonic acid derivatives[1,2] the interest on well practicable syntheses of the phosphonesterderivatives has much grown. (E)-Dialkyl-3-oxo-1-alkenylphosphonates 3, Dialkyl-1-oxo-2-alkenylphosphonates 2 and Dialkyl-1-oxoalkylphosphonates 1 are very useful structures to realize interesting transformations to various phosphonesterderivatives with a heterocyclic ring as substituent. Whereas the phosphonates 1 and 2 are well known compounds, the synthesis of the phosphonates 3 has been published only at earlier time[3]. The phosphonates 1 can be easily transformed to the hitherto unknown Dialkyl-1-bromo-1-oxoalkylphosphonates 4, useful reagents for preparing the thiazolylphosphonates 5 as well as the imidazo-[1,2-a]pyridinyl-and the imidazo-[1,2-a]-pyriminylphosphonates 6 and 7 and the indolizinderivatives 8 (scheme 1). The (E)-Dialkyl-3-oxo-1-alkenylphosphonates 3 can be brominated in a similar way to form the Dialkyl-3-oxo-1-alkenyl-4-bromophosphonates 9, which in turn enable the synthesis of the corresponding thiazolylvinylphosphonates 10, the imidazo-[1,2-a]-pyridinylvinyl- and the imidazo-[1,2-a]- pyrimidinyl-

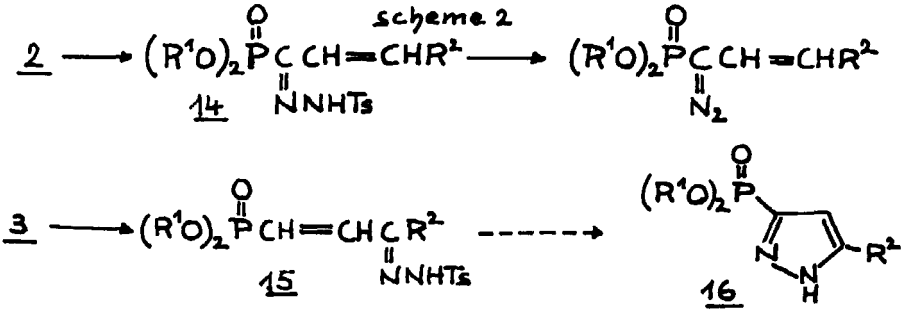
vinylphosphonates 11 and 12 as well as 13, the vinyl-analogues to the indolizinderivatives 9. Other useful

scheme 1

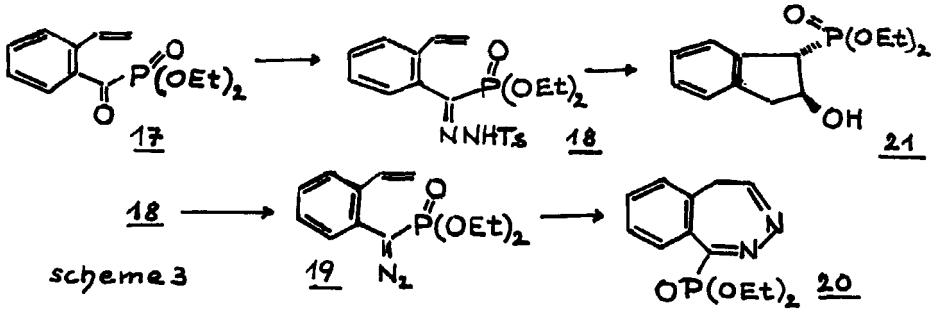


transformations of 2 and 3 consist of producing the tosylhydrazones 14 and 15 followed by basic induced formation of the corresponding diazophosphonates[4] and their cyclisation to the same type of Dialkyl-3-pyrazolyl-5-alkylphosphonates 16 (scheme 2).

scheme 2



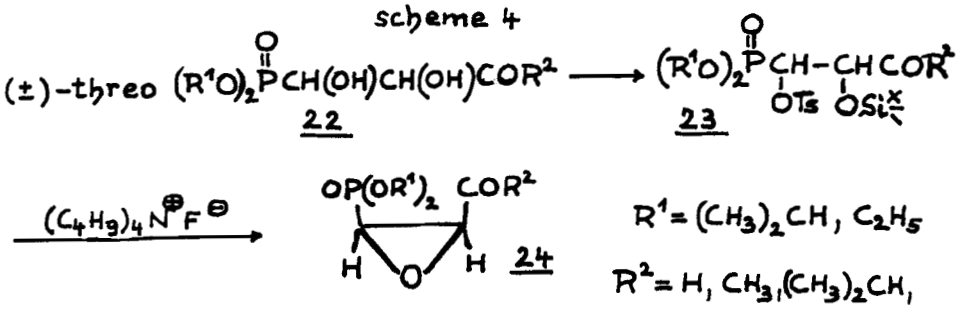
A special benzyloge to 2 is the 2-vinylbenzoylphosphonate 17 (scheme 3). It is a useful startpoint for the synthesis of the diazepinylphosphonate 20 via 18 and 19



scheme 3

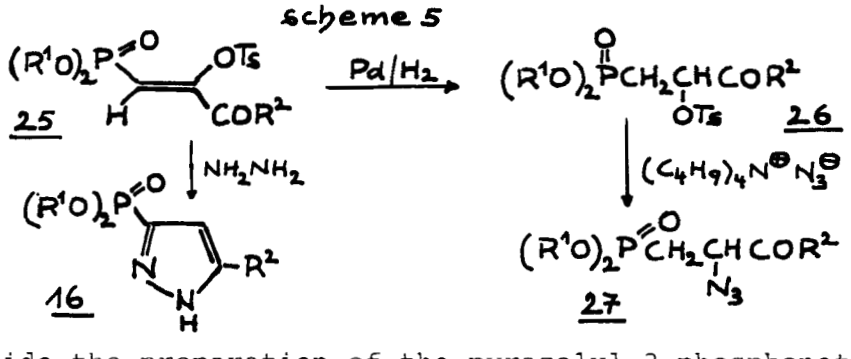
on the one and the indanylphosphonate 21 on the other hand. There are a series of other possibilities to use the compounds 3 for the synthesis of new interesting structures. The well practicable cis-hydroxylation yields the (±)-threo-glycolderivatives 22 which enable (scheme 4) the synthesis of some structural analogues 24 to the well known antibiotic phosphonomycin[5].

scheme 4



The reaction of 22 with two equivalents of tosylchloride in pyridine leads to the (Z)-enoltosylatederivatives 25 (scheme 5) a hitherto unknown substance class, which opens some approaches to other phosphonatederivatives.

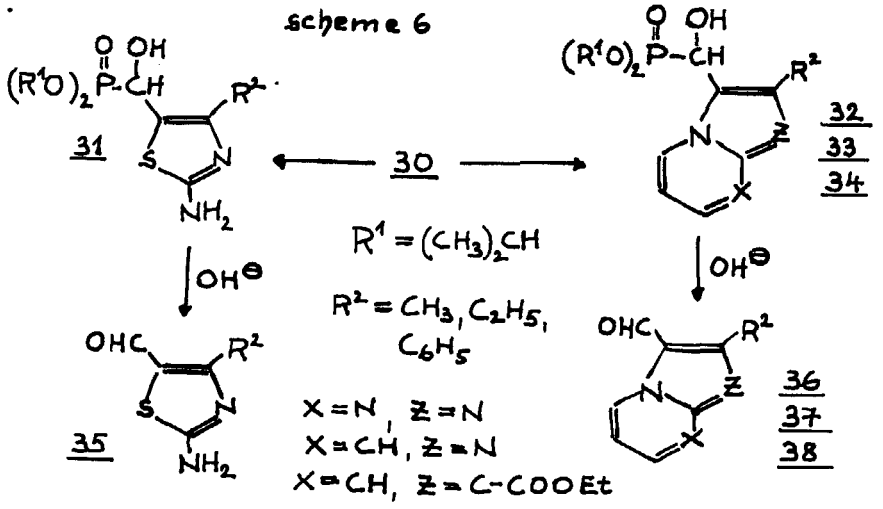
scheme 5



Beside the preparation of the pyrazolyl-3-phosphonates 16 it can be transformed by catalytic hydrogenation to the Dialkyl-2-tosyloxy-3-oxoalkylphosphonates 26. Substitution by Tetrabutylammoniumazide leads to the azidocompounds 27 a new source for the preparation of some β-Acetaminophosphonic esters. The compounds 26 can be

used also for the synthesis of the Dialkyl-5-thiazolylmethylphosphonates 28 and the imidazo-1,2-a-pyridinylmethylphosphonates 29. Another interesting approach to a series of heterocyclic structures starting from Dialkyl-3-oxo-1-alkenylphosphonates 3 consists of epoxidation to 30 (scheme 6) followed by a condensation reaction with the ambident nucleophiles thiourea, 2-aminopyridine,2-aminopyridimidine and ethyl-2-pyridylacetate[6].

scheme 6



The resulting phosphonates 31-34 are easily cleaved to diakylphosphitanion and the heterocyclic aldehyds 35-38.

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