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SYNTHESIS OF N-PHOSPHORYLATED SULPHINYL COMPOUNDS AND REACTIONS WITH VARIOUS DIENES

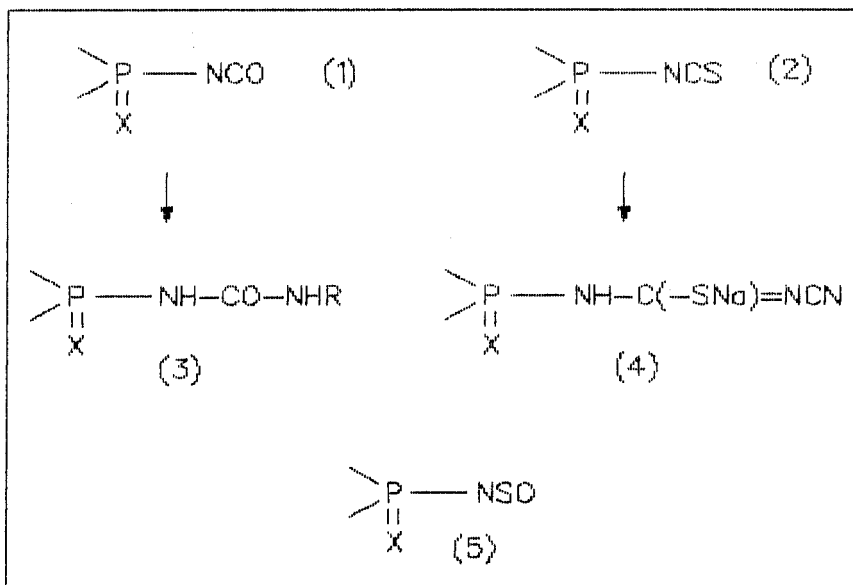
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Abstract It is reported about the synthesis and doubtless identification of the title compounds, including some cycloaddition reactions.

INTRODUCTION

In the course of our work for finding new pesticidal phosphorus compounds with better activities and better toxicological properties we used phosphoryl-substituted heterocumulenes as building blocks for syntheses in the last years. We found a new and effective way for isocyanato-phosphates (1) and for their thioanalogues (2). With the former compounds new substituted ureidophosphates (3) were obtainable [1] and with the latter special thio-ureido-derivatives, e.g. iso-thiuronium salts (4), which were interesting starting materials for heterocycles [2].



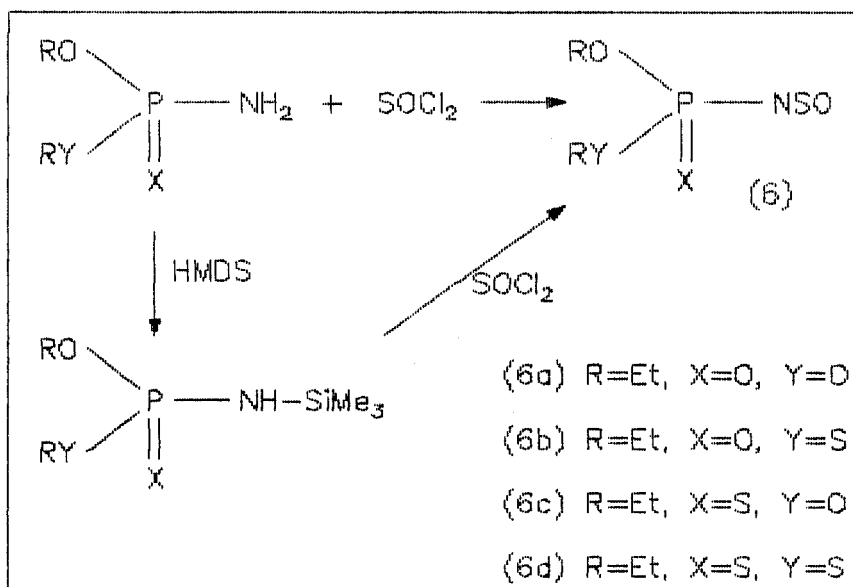
With these results as background it seemed very attractive for us to extend our investigations to compounds with pseudocumylene structures like N-sulphonyl compounds. Such substances (5) were mentioned first in the literature by Wiczorkowski [3] but the

results were not reproducible. In 1990 Meindl and Pavonic [4] reported about the synthesis of thiophosphoryl-sulphinyl esters, but without data for their characterization and without successive reactions.

RESULTS

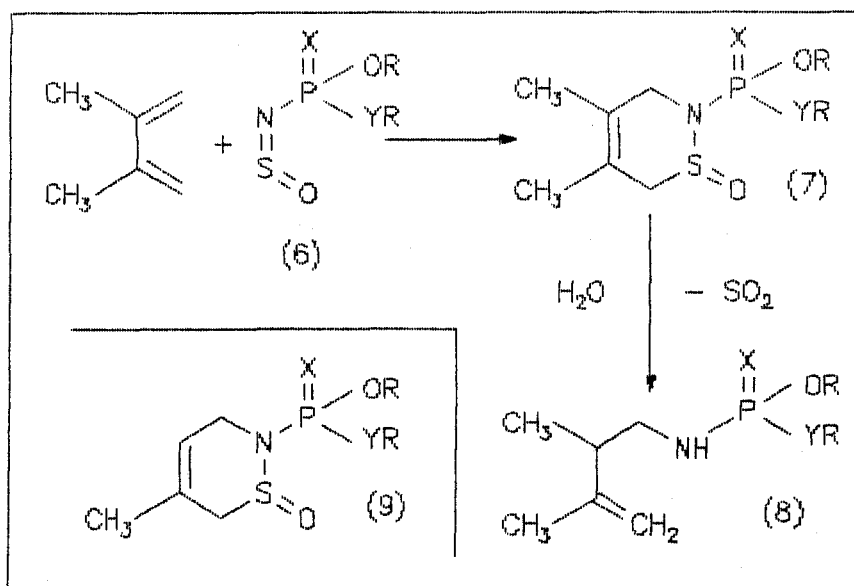
For the synthesis of NSO-compounds different methods have been developed [5]. The two most important procedures are the direct sulphonylation of amino compounds with SOCl_2 and transsulphonylations. Other methods are the application of N-lithiated materials, of trimethylsilyl-sulphinylamide or of KNSO , but they all can only be used in special cases [6]. A way from more general interest is the use of N-silylated components, because milder conditions are possible and thermal rather instable products can be obtained.

In our studies to transfer the method of direct sulphonylation with thionylchloride to amido phosphorus compounds only very complex mixtures were obtainable; the same was the case in experiments with N-sulphinyl-tosyl-amide for transsulphonylations and a number of other procedures. Only one method - in analogy to Tomaschewsky and Maniewski [7] - with the application of N-trimethyl-silyl-amido-phosphorus-O,O-diethylester showed some better results. But unfortunately the purity of the obtained N-sulphinyl-phosphorus esters has not been satisfactory, above all in respect of successive reactions. So we had to solve the problem to develop a general applicable procedure for the preparation of our desired compounds from appropriate silyl components.



We tried to prepare the N-sulphinyl compounds similar to [7] by the reaction of a silyl component with SOCl_2 . But under these conditions only mixtures of final products and starting materials could be obtained. The reason for it is a heterolytic cleavage of the N-Si-bond by the HCl formed during the reaction. Far more successful the reverse order of addition of the reaction components has been (always with an excess of SOCl_2); in these cases the heterolysis could be suppressed and the desired substances (6) were isolated in yields between 60 and 73 % (except the dithio compound). The structures were confirmed by ^{31}P -NMR-spectra [6].

A special problem was the thermal stability of the substances. Whereas the sulphur free compound (6a) proved to be rather stable at room temperature, all other compounds showed a graduated stability, which significant lowered from thio (6b) to thiono (6c) and to dithio derivatives (6d). Spectroscopical investigations showed, that in the case of (6b) gradually the more stable (6a) and diethyl-di- and tri-sulphanes were formed, in the case of (6c) also (6a) and elemental sulphur, but no sulphanes. A discussion of possible mechanisms cannot be made here, but it should be pointed out, that in the first case a dismutation of O,S- to S,S- and O,O-diethyl-phosphates is conceivable, followed by setting free of EtSH, in the second more an oxygen / sulphur exchange, followed by further reactions as well. Finally it has to be mentioned that the dithio derivative (6d) was not isolable; only mixtures of starting materials, sulphur and sulphanes could be found.



One of the aims of our work has been the application of N-sulphi-

nyl phosphorus compounds in cycloadditions. The NSO-compounds (6a)-(6c) were reacted with 2,3-dimethyl-butadiene under mild conditions (between 25 °C and 40 °C). In all cases the products were viscous, not distillable oils, which decomposed above 80 °C. For this reason the volatile components were removed at 75 °C in vacuum. The spectroscopic investigations of the remaining substances showed, that in all cases the appropriate N-phosphorylated 3,6-dihydro-1,2-thiazin-1-oxides (7) were formed. However, in all products different amounts of the open-chain N-phosphorylated 2,3-dimethyl-butenyl-amides (8) as by-products were found. The formation of them can be explained by a hydrolytic cleavage of the S-N-bond in the thiazine-cyclus and subsequent loss of SO₂. Unfortunately in no case it was possible to separate the mixtures. The determination of the components could be made by means of ¹H-noise decoupled ¹³C-NMR spectra [6].

More complex is the situation in the analogous reactions with isoprene, because the formation of two isomers (with the methyl group in 4- or 5-position) is possible. The ¹H- and ¹³C-NMR-data suggested, that in all probability only the 5-methyl isomer was formed. So - among others - the chemical shifts were in good agreement with the data of Hanson and Stockburn [8], who investigated the reaction of sulphinylamides with isoprene. Furthermore, the data for the open-chain products, found in these reactions too, were only explainable with structure (9). That means, that the reactions of our sulphinylamides with dienes showed a high regioselectivity. In this respect it has to be mentioned, that results of MNDO calculations [9] on various model substances were consistent with the observed reactivity of our compounds.

The analogy of (6) to the phosphorylated heterocumulenes (1) and (2) is very low. But they show a series of interesting synthetic possibilities, so for the introduction of phosphorus groups in heterocyclic systems, a method, which should be expanded. But their chemistry cannot also be seen in a very analogy to other sulphinyl compounds. The reason for it is the strong and characteristic influence of the P-moiety to the NSO-group.

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