

PL 1

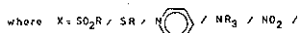
A NEW SYNTHESIS OF 5-NITROFURYLETHYLENE COMPOUNDS

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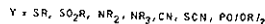
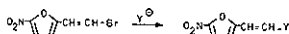
The methods of synthesis known up to this date of 5-nitrofuryl-ethylene derivatives give possibilities of preparing only some types of these compounds. The new found ways in this area enabled to synthesise new type of 5-nitrofuryl-ethylene compounds.

The first way is based on the use of the acidic hydrogens of some nitrofuryl derivatives in the condensation reactions with carbonyl compounds.



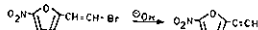
This method is suitable for preparing three and foursubstituted 5-nitrofuryl-ethylene derivatives. The modified Horner-Wittig reaction on suitable ketone was used in the case, when X was an electrondonating group.

The second way is more common and give possibilities to prepare unknown compound of 5-nitrofuryl-ethylene series. This method is based on the use of 5-nitrofurylvinylbromide (I) in the nucleophilic vinylic substitution reaction, where the reagents are compounds containing a free electron pair

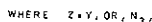
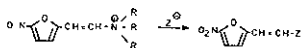


nitrogen heterocycles and so on

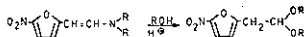
The elimination of HBr goes by the action of strong bases on I and the 5-nitrofurylacetylene arises.



The use of 5-nitrofurylvinylammonium salts is more advantageous while the reaction proceeds in polar solvent and this compound reacts with more reagents than compound I.



The enamines of 5-nitrofuryl-ethylene type are the potential source for preparation of derivatives of unknown 5-nitrofuryl-acetaldehyde



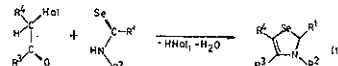
PL 2

RINGSCHLUSSREAKTIONEN AN SELENOCARBONAMID-DERIVATIVEN ZU 1,3-SELENAZOLEN, 1,3,4-SELENADIAZINEN UND 1,3,4-SELENADIAZOLEN

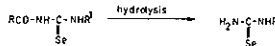
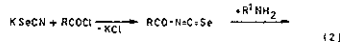
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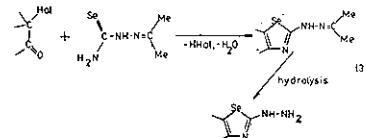
Selenazoles are the selenium analogues of thiazoles, and although the first derivatives of 1,3-selenazole were prepared by Hofmann as early as 1889, only a few publications on this subject have appeared in the literature until now. Hofmann was a student of Hantzsch's and transferred his thiazole synthesis to the selenazoles. This most useful and versatile of all the thiazole syntheses is the reaction of an α -halo ketone or aldehyde with a thioamide. For his purpose Hofmann used selenourea instead of thioamide. Even nowadays this method is still the most usual one. It permits a wide variety by choosing suitable reaction partners as to be seen in formula 1.



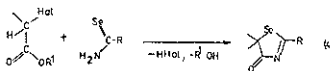
The selenoureas, needed for condensation, can usually be prepared by addition of hydrogen selenide to a solution of the corresponding cyanamides or carbodilimides. They can be less dangerously and quite smoothly synthesized according to Douglas via the isoselenocyanates by the alkaline hydrolysis of the corresponding acyl-substituted selenoureas (formula 2).



2-Hydrazinoselenazoles have been prepared by the use of selenosemicarbazide as selenocarbonamide. Starting from acetone selenosemicarbazone one can prepare the 2-isopropylidenehydrazinoselenazoles in a smooth reaction by condensation with α -halocarbonyl compounds. Their careful acidic hydrolysis leads to the free 2-hydrazino-selenazoles (formula 3).



On the other hand, the α -halocarbonyl component offers the possibility of variation too. For instance, α -halocarboxylic acids, or rather their esters, form derivatives of 4-oxoselenazoline (formula 4).



First investigations on the reactivity of the 1,3-selenazoles were undertaken by Haginiwa. He came to the conclusion that the 5-position of selenazoles is slightly reactive towards electrophilic substitution. This reactivity is still further increased by substituents in the 2-position, which can exert the +M-effect. We found during our investigations multiple nitration depending on the conditions of the reaction and the substrate, whereas Haginiwa only described the formation of the 5-nitro derivatives. Thus, the 2-benzamino-4-ary(alkyl)selenazoles form the corresponding 5-nitro derivatives under mild conditions using the nitrate/sulfuric acid method. The use of cold mixed nitric and sulfuric acids also effects the phenyl groups which may be present, leading to dinitro or trinitro compounds (formula 5).