SALTS OF N-IMIDOYLHETEROAROMATIC CATIONS

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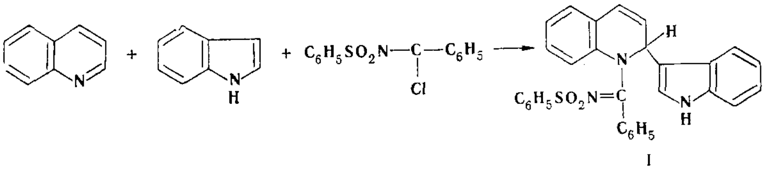
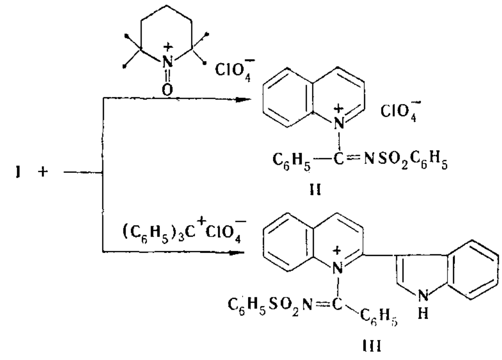
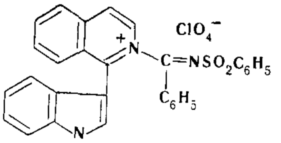
UDC 547.288.3'752'831.1'833.1.9

Salts of N-imidoylheteroaromatic cations have not been described. Their preparation by the direct reaction of imidoyl chlorides with pyridines and other bases is extremely difficult because of the instability of the resulting salts and the development of side products. We have developed a universal method for the preparation of substituted and unsubstituted N-imidoylbenzopyridinium salts that includes two steps. The first step is the production of N-imidoyl derivatives of dihydroheteroaromatic compounds by the reaction of pyridines or other N-heteroaromatic compounds with nucleophiles (for example, indole) in the presence of imidoyl chlorides [1]:

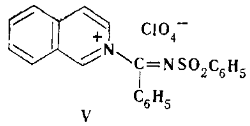


The second step consists in aromatization of I under the influence of various aromatizing agents; in this case one observes either the formation of N-imidoyl salts II and V with detachment of the nucleophilic substituent, orthe formation of salts III and IV with retention of this substituent:





IV



V

We used this method to obtain 1-phenylsulfonylbenzimidoylquinolinium perchlorate (II), with mp 178-180°C, in 52% yield and 1-phenylsulfonylbenzimidoyl-2-(3-indolyl)quinolinium perchlorate (III), with mp 185-187°C, in 60% yield.

In contrast to this, 2-phenylsulfonylbenzimidoylisoquinolinium perchlorate (V) (82%, mp 163-165°C) and 1-(3-indolyl)-2-phenylsulfonylbenzimidoylisoquinolinium perchlorate (42%, mp 136-139°C), respectively, were obtained by the action of triphenylmethyl perchlorate and 1-oxo-2,2,6,6-tetramethylpiperidinium perchlorate on 1-(3-indolyl)-2-phenylsulfonylbenzimidoyl-1,2-dihydroisoquinoline. The structures of I-V were confirmed by the IR, PMR, and mass spectra, and the results of elementary analysis are in agreement with the calculated values. Ami-

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Dnepropetrovsk Construction-Engineering Institute, Dnepropetrovsk 320631. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 6, pp. 840-841, June, 1983. Original article submitted June 21, 1982.

0009-3122/83/1906-0680$07.50

dine, with mp 147°C (mp 148°C [2]), and the corresponding base were isolated in the reaction of salts II-V with aniline.

The method described above can be used for the synthesis of pyridinium and imidazolium salts and salts of other heterocyclic cations with an imidoyl residue attached to the nitrogen atom.

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SIMPLE SYNTHESIS OF 1-AMINOTETRAZOLE

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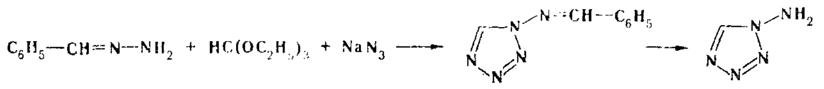
UDC 547.796.1.07

Tetrazoles are promising substances for a number of purposes [1]; however, many of them (even the simplest, including 1-aminotetrazole) are still difficult to obtain and have not been characterized very well.

The direct amination of tetrazole with hydroxylamine-O-sulfonic acid gives the product in low yield and is complicated by the formation of a mixture of two isomers, the separation of which is hazardous because of the increased dangerously explosive character of 2-aminotetrazole [2]. A multistep method of synthesis, according to which the corresponding imido ester is obtained from benzaldehyde hydrazone and an ortho ester at 140°C, and the product is cyclized with NaN_3 in the course of 24 h, is more convenient. However, the latter method is time consuming, and requires a threefold to fourfold excess of the ortho ester and sodium azide, and the overall yield of 1-aminotetrazole is 37% [3]. We have studied the possibility of the one-step realization of this reaction and have found that in acetic acid the reaction of benzaldehyde hydrazone, ethyl orthoformate, and sodium azide proceeds readily at 75-85°C and is complete in 2.5 h with the formation of 1-benzylideneaminotetrazole, the hydrolysis of which gives 1-aminotetrazole in 60-62% yield:



The method of synthesis can be used for the simple and rapid preparation of N-substituted 1-aminotetrazoles from the corresponding aryl(alkyl)hydrazines.

A 250-ml sample of acetic acid was added with stirring to a mixture of 60 g (0.5 mole) of benzaldehyde hydrazone, 39 g (0.6 mole) of NaN_3, and 150 ml (0.9 mole) of ethyl orthoformate, and the mixture was heated at 75-85°C for 2.5 h. It was then poured with stirring into 1.3 liters of water, and the precipitate was removed by filtration and washed with water. Water (250 ml) and 120 ml of concentrated hydrochloric acid were added to the reaction product, and the benzaldehyde was removed by steam distillation. The residue was neutralized and evaporated, and the residue was extracted with ethyl acetate. The extract was dried with $MgSO_4$, and the solvent was removed by distillation to give 26.2 g (62%) of 1-aminotetrazole in the form of a clear yellowish liquid (n_D^{20} 1.5140, d_4^{20} 1.363) that crystallized upon prolonged cooling to 0°C to give colorless acicular crystals with mp 8-10°C. IR spectrum (thin layer): 975, 1105, and 1190 (ring δ); 1623 (δ NH_2); 3155 (νCH); 3215 and 3340 cm^{-1} (νNH_2). PMR spectrum (DMSO): 7.05 (s, 2H, NH_2) and 9.16 ppm (s, 1H, CH). The benzaldehyde derivative had mp 92-93°C, in agreement with the literature value [3]. 1-Aminotetrazole explodes under pronounced friction and upon impact.

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0009-3122/83/1906-0681$07.50