SYNTHESIS OF 1,3-DIGLYCIDYLIMIDAZOLIUM SALTS

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For the first time, 1,3-diglycidylimidazolium salts were obtained. Their synthesis was accomplished by two routes: the reaction of imidazole with epichlorohydrin in the presence of sodium perchlorate with the subsequent dehydrochlorination of the reaction products with alkalis, and the quaternization of 1-glycidylimidazoles with epichlorohydrin in the presence of salts of strong acids.

In the works [1, 2], we first obtained stable glycidylazolium and glycidylazinium salts by the recyclization of the oxirane ring of epichlorohydrin by the action of azoles and azines in the presence of sodium perchlorate. However, the isolation of difunctional oxirane-containing salts remained problematic in connection with the probability of oligomerization, which is higher by comparison with monofunctional systems, as well as the high sensitivity of the N,N'-disubstituted imidazolium cation obtained to alkaline agents.

We previously established that the reaction of imidazole (Ia) with epichlorohydrin in an alcoholic medium leads to the formation of the chlorohydrin derivative of imidazole (II), the further exposure of which results in conversion to ionic oligomers [3]. However, the character of the reaction changes in the presence of sodium perchlorate: 1-glycidylimidazolium hydroperchlorates (III) are formed initially, and these undergo the further addition of a second molecule of epichlorohydrin to give the mixed glycidylchlorohydrin salt (IV) (see Scheme 1, route 1). The last is not isolated in the crystalline form, but its formation is confirmed by the analysis of the resin-forming reaction product for the content of epoxide groups (CEG) and the content of readily hydrolyzed chlorine.

The formation of the intermediate imidazolium salt (IV) may also proceed by another route — via the chlorohydrin derivative (II) with its subsequent quaternization by epichlorohydrin in the presence of sodium perchlorate. The role of the last consists in the removal of the nucleophilic chloride ion, able to initiate the chain of polymerization of the oxirane rings in solution, from the sphere of reaction (in the form of sodium chloride precipitated from the epichlorohydrin), as well as the stabilization of the final glycidylimidazolium salt (Va).

By analogy with the reaction of hydroperchlorates of pyridines described in the work [4], as well as the conversion of hydroperchlorates of 2-methylbenzimidazole (Id). HClO₄ and 3,5-dimethylpyrazole by the action of epichlorohydrin, presented here, to the bischlorohydrin salts (VII) and (VIII), the addition of epichlorohydrin to salts of the type (III) is also evidently characteristic of hydrosalts of azaaromatic rings. The synthesis of compound (VII) evidently also proceeds via the intermediate hydroperchlorate (VI).

The action of equimolar amounts of alkalis on the intermediate (IV) allows the isolation of the diglycidylimidazolium salt (Va) in the form of a colorless crystalline substance, which is very stable on storage (the period of storage without significant change of the CEG is not less than 1 year when the Δ CEG/CEG ≤ 10%), and crystallizes from polar solvents (alcohols, without the noticeable opening of the epoxide groups).

The isolation of the aromatic substituted imidazolium salts (Vb,c) was found to be effective by the route 2 (see Scheme 1) based on the quaternization of the 1-glycidylimidazoles (IXa,b) with epichlorohydrin, previously described [5], in the presence of sodium perchlorate. The reaction proceeds exclusively readily even at room temperature for (IXb), or with moderate heating at 50-60°C, for (Xa). The salt (Vb) is isolated in the crystalline form, and (Vc) is isolated in the form of a colorless luminescing oil-forming product with the CEG close to the calculated value.
The exchange of anions in the salts obtained can be performed by the method of [2], described for glycidylazinium salts, using potassium salts of inorganic and organic acids in methanol or water. However, a disadvantage of the approach indicated is that this case requires the good solubility of both salts in the solvents indicated and the precipitation of one of the exchange products in the residue; this is not always practicable. Moreover, the separation of oxirane-containing salts from water is not always expedient due to the hydrolysis of three-membered rings.

Taking into account the simplicity and ease in performing the quaternization of the glycidylimidazole (IXb), we attempted to synthesize salts with weakly nucleophilic counterions (BF₄, ClO₄) using the reaction in the diphasic system of epichlorohydrin — the aqueous solution of the inorganic salt. Thus, when the 1-glycidylimidazole (IXb) reacts with epichlorohydrin in the presence of a saturated solution of sodium tetrafluoroborate, the salt (Vc) (W = BF₄) is isolated from the organic phase in the form of a colorless luminescing oil-forming product with a high CEG close to the calculated value. By analogy, the perchlorate (Vc) (W = ClO₄) is also obtained. It can be seen that the diphasic approach of the method can be extended to the synthesis of glycidylimidazolium salts with other counterions, which are however more strongly nucleophilic, as well as proton-containing anions (Cl⁻, CH₃COO⁻, H₂PO₄⁻, etc.) which are not inert to epoxide groups, and we could not isolate the pure salts in this case.

It is interesting that the salts (Vc) (W = BF₄, ClO₄), especially the tetrafluoroborate, undergo ready self-hardening on heating at 100-130°C for 0.5-1 h to form luminophore polymers. This property is not characteristic of the salt (Vb); this is probably associated with the absence of the sufficiently acidic mesoproton C²H in its structure which can be cleaved on heating to form the borohydrofluoric or perchloric acids correspondingly and the corresponding heteroaromatic carbene, catalytically strengthening the monomer (Vc).

The attempt to carry out the analogous reaction of epichlorohydrin with azines (pyridines, acridine) in a diphasic system leads to the hydrolysis of the epoxide groups and the formation of N-(2,3-dihydroxypropyl)azinium salts, in contrast to the smooth conversion in the dry medium according to [2].

Therefore, we developed two new approaches to the synthesis of previously unknown diglycidylimidazolium salts, based on the reaction of the corresponding N-unsubstituted imidazoles and N-glycidylimidazoles with epichlorohydrin in the presence of anions of strong acids.