PRODUCTION OF ALKALI SALTS OF 2-PHENYLIMINO-4-TRIAZOLIDINONE

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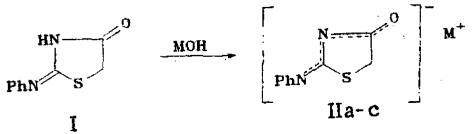
Alkali salts of 2-phenylimino-4-thiazolidinone were produced by mixing an acetone solution of it over granulated alkali.

The 2-phenylimino-4-triazolidinone anion (I) is a unique object for the study of the dual reactivity of ambident anions [1]; however, the production of salts of this compound pure enough for investigation of reactivity involves great difficulties. When the compound I is dissolved in 5-20% aqueous alkali at 80°C, followed by cooling of the solution, the salts obtained [2] are contaminated as a result of instability of the thiazolidine ring under these conditions [3]. A solvent for the recrystallization of the salt cannot be selected.



I

IIa-c

II a M=Na; b M=K; c M=Cs

We found that the salts IIa, b exist in two crystalline forms, one of which is soluble in acetone, while the second is insoluble. Thus, the sodium salt IIa, obtained from aqueous alkali (first crystalline form), dissolves in acetone, but 2-3 min after it dissolves, an abundant precipitate of a second crystalline form, which is indistinguishable from the first form in spectral characteristics (UV, IR, and PMR spectra) and temperature of decomposition, begins to separate out of the entire volume of the solution.

The method that we proposed consists of mixing a solution of the compound I in acetone over granulated alkali until a precipitate of the salt II is formed. Probably an acetone-soluble form is first produced and then is converted to an insoluble form, which precipitates from the solution. The salt obtained on the interface can pass into the solution and be uniformly distributed in its volume as a result of the mixing until it begins to precipitate from the solution, as a result of which the surface of the alkali granules is not blocked by a deposit of the salt obtained, and access of compound I from the solution to the surface of the alkali is unhindered. When the reaction is conducted under the indicated conditions in non-aqueous medium and at room temperature, no hydrolytic decomposition of the salt occurs; it is obtained in a high degree of purity and does not require additional purification. According to the data of potentiometric titration of a sample of the salt obtained, salt formation proceeds to an extent of 99-100%. The yield of the salt is increased to ~50% in comparison with 30-40% in production from aqueous alkali according to the method of [2].

The cesium salt IIc could be obtained only by the proposed method: in an attempt to produce it according to the method of [2] it did not precipitate from the aqueous solution.

EXPERIMENTAL

The PMR spectrum was recorded in DMSO-D_6 on a Perkin-Elmer 12 instrument (60 MHz), internal standard HMDS; the IR spectra were recorded on a IKS-29 spectrophotometer in tablets of KBr, the UV spectra on an SF-16 spectrophotometer in ethanol. Potentiometric titration was performed on a pH-121 pH meter with glass and silver chloride electrodes. A weighed sample of the salt (10^{-4} mole) was dissolved in 20 ml of methanol, using a 0.1 N solution of hydrogen chloride in methanol as the titrant.

Sodium Salt of 2-Phenylimino-4-thiazolidinone (Ia). A solution of 1.0 g (0.005 mole) of compound I in 100 ml of acetone, purified by redistillation over 3 Å molecular sieves, was

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mixed with 1.2 g (0.03 mole) granulated sodium hydroxide for 40-50 min until a voluminous precipitate of the salt IIa formed, after which mixing was continued for another 10-15 min. The reaction mixture was removed by decanting from the alkali granules, the salt was filtered off and dried under vacuum (1-2 mm Hg, 100°C) over 3 Å molecular sieves to constant weight. Yield 0.54 g (50%), t. decomp. 250-252°C. UV spectrum, λ_{max} (log ε): 265 nm (4.22). IR spectrum: 1645 (C), 1620 (CN), 1530 cm^{-1} (CN). PMR spectrum, δ: 7.09-7.57 (m, Ph), 3.77 ppm (s, 5H). Found: C 51.0; H 3.4; N 13.0; S 14.8%: $C_9H_7N_2NaOS$. Calculated: C 50.5; H 3.3; N 13.1; S 15.0%.

Potassium Salt of 2-Phenylimino-4-thiazolidinone (Ib). Produced analogously to compound Ia. Yield 0.67 g (60%), t, decomp. 250-253°C. UV spectrum, λ_{max} (log ε): 265 nm (4.22). IR spectrum: 1635 (CO, CN), 1545 (CN), 1520 cm^{-1} (CN). Found: C 47.2; H 3.5; N 11.8; S 13.6%. $C_9H_7KN_2OS$. Calculated: C 46.9; H 3.1; N 12.2; S 13.9%.

Cesium Salt of 2-Phenylimino-4-thiazolidinone (Ic). Produced analogously to compound Ia. Yield 0.67 g (40%), t. decomp. 220-230°C. IV spectrum, λ_{max} (log ε): 265 nm (4.20). IR spectrum: 1640 (CO), 1610 (CN), 1550 (CN), 1540 cm^{-1} (CN). Found: C 33.1; H 2.6; N 8.6; S 9.9%. $C_9H_7CsN_2OS$. Calculated: C 33.4; H 2.2; N 8.6; S 9.9%.

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SYNTHESIS AND STRUCTURE OF 1,1-DIOXIDES OF 3-ALLYL(STYRYL)-4H-1,2,4-BENZOTHIADIAZINE

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541.62:543:422.4

The reaction of o-aminobenzenesulfonamides with acids of crotonic and cinnamic acids in dioxane yielded the corresponding anilides, which were cyclized to derivatives of 1,2,4-benzothiadiazine 1,1-dioxide. The structure of the end products is discussed in connection with the possibility of tautomeric equilibrium of the 2H- and 4H-forms on the basis of the spectral data.

Derivatives of benzothiadiazine, which contain an alkenyl substituent in the 3-position of the heterocyclic ring, possess pronounced hypotensive activity [1, 2], comparable with the action of diazoxide in clinical use [3]. According to the spectral data [4, 5], and quantum chemical calculations [6], 1,1-dioxides of 1,2,4-benzothiadiazine exist primarily in the 4H-form. In view of this it is of interest to evaluate the influence of a substituent with a multiple bond on the state of the tautomeric equilibrium.

For this purpose we synthesized some 1,1-dioxides of 3-allyl(styryl)-4H-1,2,4-benzothiadiazine (IIIa-d) by heterocyclization of o-sulfamoylanilides of crotonic and cinnamic acids (IIa-c) under the action of alkali (Table 1). The anilides II in turn were produced from o-aminobenzenesulfamides (Ia-d) and chlorides of crotonic and cinnamic acids in dioxane. Since the N-methylcrotonanilide IId is hydrolyzed in alkaline medium to the initial o-N-methylaminobenzenesulfamide (Id), thermal cyclization of the anilide IId was used to synthesize the dioxide IIId.

The structure of compounds IIa-d was confirmed by spectral data. It should be noted that the frequencies of the stretching vibrations of the C=C and C=O bonds in the IR spectrum of compound IIc are shifted in the low-frequency direction in comparison with croton-

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