LETTERS TO THE EDITOR

USE OF o-HYDROXYAMINOBENZOIC ACID FOR THE PREPARATION OF HETEROCYCLIC COMPOUNDS

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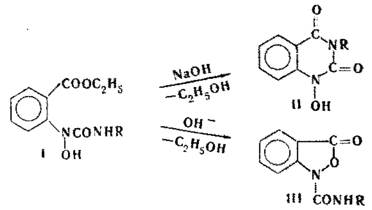
Anthranilic acid and its derivatives are widely used for the synthesis of nitrogen-containing benzoheterocycles, while its analog o-hydroxyaminobenzoic acid has been used only to prepare unsubstituted 2,1-benzoisoxazolone |1|.

Furthermore, methods for the synthesis of 3-hydroxyquinazoline-2,4-diones and 1-hydroxyquinolin-2-ones are well known, but no general method has been proposed for the synthesis of the 1-hydroxyquinazoline-2,4-diones related to them, and it is only recently that a compound of this type has been obtained |2|. Derivatives of o-hydroxyaminobenzoic acid may be used for the synthesis of benzo-N-heterocycles containing an OH group in position 1. Thus, the esters of N-alkyl(aryl)carbamoyl-o-hydroxyaminobenzoic acid (I) that we have obtained can readily be cyclized to form 3-substituted 1-hydroxyquinazoline-2,4-diones (II). N-Carbamoyl-2,1-benzoisoxazolones (III), which have not been described in the literature, can be obtained from I just as easily.



The direction of cyclization is determined not so much by the nature of the cyclizing agent as by its quantity and concentration and the conditions under which the reaction is performed. The reaction of excess 5–25% aqueous alkali with solid I rapidly produces compound II in the form of a salt. On acidification, II when R = C_6H_5, m-ClC_6H_4, 3,4-$Cl_2C_6H_3$, or furfuryl (mp 183.5–184.5, 220, > 260, 220–221° C, respectively) are obtained with yields of 90–98%. For II, when R = CH_3, C_2H_5, $CH_2{=}CHCH_2$ (mp 231–232, 175.5–176.5, and 148–149° C, respectively) the yield does not exceed 60–75% because of the formation of unsubstituted, 2,1-benzoisoxazolone (readily washed out with ether) as a by-product. In these reactions the carbamoyl group is split out, and on acidification there is a vigorous evolution of CO_2.

Compounds II when R represents an alkyl group containing more than three C atoms could not be obtained. The structure of the compounds II was confirmed by their analysis, reactions, and IR spectra: ν_{CO} 1705–1730 and 1660–1670 cm^{-1} (in $CHCl_3$), characteristic bands for quinazolinediones |3| at 1480–1510 and 1595–1615 cm^{-1}, but no ν_{NH} band, and a band at 3150–3200 cm^{-1} corresponding to an OH group bound by an intramolecular hydrogen bond (no change when a solution in CCl_4 is diluted). The presence of an OH group is also confirmed by the formation of a violet coloration with $FeCl_3$, and by alkylation and acylation reactions.

In ethanolic solution in the presence of catalytic amounts of caustic alkali (at 40–60° C for 1–2 hr), triethylamine, or water compounds I are converted in a yield of 90–100% into III (R = CH_3, allyl, C_6H_5, tert-C_4H_9, with mp 137–138, 98.5–101, 148–151, and 97–98° C, respectively). The structure of compounds III is confirmed by their IR spectra: ν_{CO} 1775–1785 cm^{-1} (as for unsubstituted benzoisoxazolone) and 1715–1730 cm^{-1}, ν_{NH} 3440–3470 cm^{-1}. The alkaline hydrolysis of III leads to the splitting out of the carbamoyl group and the formation of 2,1-benzoisoxazolone.

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