SYNTHESIS OF 4H-1,3-BENZOXAZIN-4-ONIUM SALTS AND 4H-1,3-BENZOXAZIN-4-ONES

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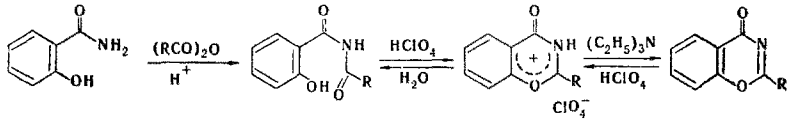
We have found that 4H-1,3-benzoxazin-4-onium perchlorates (I) can be readily obtained by acylation of salicylamide with aliphatic carboxylic acid anhydrides in the presence of perchloric acid. The reaction apparently proceeds through the intermediate formation of N-acylsalicylamides (II), which are actually cyclized in acetic acid by the action of $HClO_4$. Protonation of 4H-1,3-benzoxazin-4-ones (III) also gives salts I. In addition, salts I are convenient starting materials for the synthesis of III (by treatment of perchlorates I with dry triethylamine). The reaction of salts I with water gives II in quantitative yields.



IIb Ia,b IIIa,b

I, III a R = CH_3; I-III b R = C_6H_5

EXPERIMENTAL

2-Methyl-4H-1,3-benzoxazin-4-onium Perchlorate (Ia). A 5-ml sample of 70% perchloric acid was added to a mixture of 6.85 g (0.05 mole) of salicylamide and 30 ml of acetic anhydride, and the precipitated crystals were removed by filtration and washed with ether to give 12.8 g (98%) of salt Ia with mp 208° (from acetic acid). IR spectrum: 1773, 1640, 1600, 1587, and 1540 cm^{-1}. Found: C 41.2; H 3.3; Cl 13.0; N 5.2%. $C_9H_7NO_2 \cdot HClO_4$. Calculated: C 41.4; H 3.1; Cl 13.6; N 5.4%.

2-Phenyl-4H-1,3-benzoxazin-4-onium Perchlorate (Ib). This compound, with mp 247° (from acetic acid-nitromethane), was obtained in 75% yield by cyclization of II (R = C_6H_5). IR spectrum: 1772, 1632, 1603, 1573, and 1516 cm^{-1}. Found: C 52.2; H 3.3; Cl 11.3; N 4.0%. $C_{14}H_9NO_2 \cdot HClO_4$. Calculated: C 52.0; H 3.1; Cl 11.0; N 4.2%. Perchlorate Ia was similarly obtained in 97% yield.

2-Phenyl-4H-1,3-benzoxazin-4-one (IIIb). A 1.01-g (0.01 mole) sample of dry triethylamine was added to 3.23 g (0.01 mole) of perchlorate Ib, after which the mixture was extracted with benzene, and the benzene extract was evaporated to give 2.23 g (100%) of IIIb with mp 100-102° (from cyclohexane) [1]. Compound IIIa, with mp 217° (from benzene), was similarly obtained in 95% yield [2].

LITERATURE CITED

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2. T. Hanada, Bull. Chem. Soc. Japan, 31, 1024 (1959); Chem. Abstr., 53, 18,042 (1959).

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