

anhydride for 10 min, after which 0.08 g (1 mmole) of sodium acetate was added, and the mixture was refluxed for another 30 min. It was then cooled, diluted with water, and allowed to stand for 24 h. The resulting solid was removed by filtration to give 0.2 g (43%) of a product with mp 70°. IR spectrum: 1750, 1720, 1665, and 1600  $\text{cm}^{-1}$ . Found: C 75.8; H 6.0%.  $\text{C}_{28}\text{H}_{26}\text{O}_5$ . Calculated: C 76.0; H 5.9%.

B) A 0.18g (1 mmole) sample of sodiomalonic ester was added to a suspension of 0.4 g (1 mmole) of 2,4-diphenyl-6- $\delta$ -ethoxydivinylpyrylium perchlorate in dry ether, and the resulting sodium perchlorate was removed by filtration after a few hours. The ether was removed from the filtrate by distillation, and the residue was refluxed in acetic anhydride for 10-15 min. The mixture was diluted with water and extracted with ether, and the ether layer was dried with sodium sulfate. The ether was removed by distillation to give a product identical to the product obtained by method A.

#### LITERATURE CITED

1. M. F. Shostakovskii, Simple Vinyl Ethers [Russian translation], Mir (1952).
2. W. Dilthey and J. Fischer. Chem. Ber., 57, 1653 (1924).

#### ACYLATION OF SALICYLNITRILE AND SALICYLALDOXIME AS A METHOD FOR THE SYNTHESIS OF 4H-1,3-BENZOXAZIN-4-ONIUM SALTS

G. N. Dorofeenko. Yu. I. Ryabukhin,  
and V. V. Mezheritskii

UDC 547.867.2.07:542.951.1

Methods were developed for the synthesis of 4H-1,3-benzoxazin-4-onium salts by acylation of salicylnitrile and salicylaldehyde with acid anhydrides and chlorides in the presence of perchloric acid or tin perchlorate.

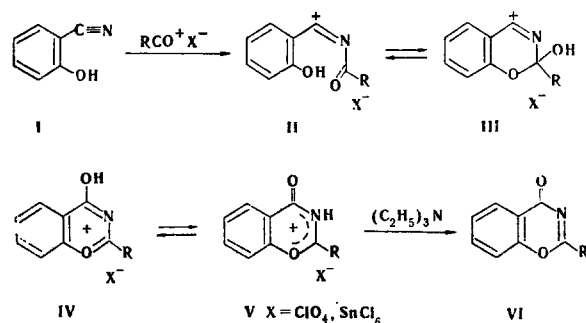
In the present research, which is a continuation of our research on the synthesis of 4H-1,3-benzoxazin-4-onium salts [1], we have shown that 4H-1,3-benzoxazin-4-onium perchlorates (V) are formed in the acylation of salicylnitrile (I) with aliphatic acid anhydrides (acetic, propionic, butyric, valeric, and caproic) in the presence of equimolar amounts of 70% perchloric acid. The reaction proceeds under mild conditions when perchloric acid is added to a solution of nitrile I in excess acid anhydride. The yields of the salts increase when the mixtures are heated to the boiling point. The benzoxazinonium salts can also be obtained by acylation of nitrile I with carboxylic acid chlorides in the presence of tin perchlorate. The initially formed hexachlorostannates of V ( $\text{X} = \text{SnCl}_6$ ) are readily converted to the corresponding perchlorates. The structure of hexachlorostannate V ( $\text{R} = \text{C}_6\text{H}_5$ ) was confirmed by conversion to the previously known 2-phenyl-4H-1,3-benzoxazin-4-one (VI) by treatment with triethylamine.

Nitrilium salt II [2] is evidently formed initially in the acylation of salicylnitrile with both acid anhydrides and chlorides; II then undergoes tautomerization to cyclic cation III, which is subsequently rearranged to hydroxyazapyrylium salt IV. The latter, which is less thermodynamically favorable [3], is converted to oxazinonium salt V:

---

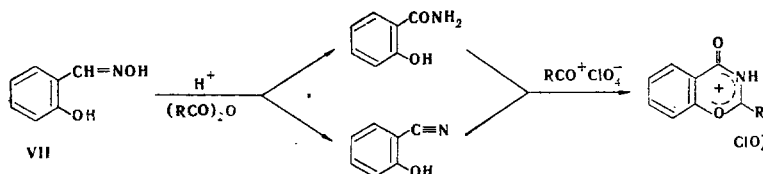
Rostov State University. Scientific-Research Institute of Physical and Organic Chemistry, Rostov-on-Don. Translated from Khimiya Geterotsiklicheskikh Soedinenii. No. 6, pp. 742-744, June, 1976. Original article submitted July 7, 1975.

*This material is protected by copyright registered in the name of Plenum Publishing Corporation, 227 West 17th Street, New York, N.Y. 10011. No part of this publication may be reproduced, stored in a retrieval system, or transmitted, in any form or by any means, electronic, mechanical, photocopying, microfilming, recording or otherwise, without written permission of the publisher. A copy of this article is available from the publisher for \$7.50.*



The acylation of salicylnitrile can be realized with aliphatic acids in the presence of tin perchlorate to give salts V, but the yields in this case do not exceed 30%. The reaction probably proceeds via the mechanism of acylation of nitriles with organic acids recently proposed in [4]. When molar amounts of an acid chloride (acetyl chloride or benzoyl chloride) are added to the reaction mixture, the yields of the salts increase to 65%, but the added chloride itself does not enter into the acylation reaction under these conditions. Thus 2-methyl-4H-1,3-benzoxazin-4-onium perchlorate rather than 2-phenyl-4H-1,3-benzoxazin-4-onium perchlorate is obtained when salicylnitrile, benzoyl chloride, and tin perchlorate are refluxed in excess acetic acid. Salts V ( $\text{R} = \text{C}_2\text{H}_5$ ) were similarly synthesized from acetyl chloride and propionic acid. The formation of a mixture of salts was not observed in this case (the mixture was monitored by chromatography on Silufol UV-254 plates). The role of the added acid chloride probably reduces to the formation of an acid chloride in which the components are refluxed, and which subsequently acylates nitrile I.

Salicylaldoxime (VII) can be used as the starting compound for the synthesis of benzoxazinonium salts. In this case Beckmann rearrangement leading to the formation of salicylamide [5], which is subsequently acylated by our previously proposed scheme [3], precedes the formation of benzoxazinonium salts. Dehydration of salicylaldoxime to salicylnitrile is also possible [6], but the data on the yields of benzoxazinonium perchlorates (86–95%) constitute evidence in favor of the first assumption.



Acylation of the phenolic hydroxyl group of salicylnitrile and salicylaldoxime by acid anhydrides and subsequent cyclization with splitting out of the acid are possible under the reaction conditions.

## EXPERIMENTAL

The IR spectra of mineral oil suspensions of the compounds were recorded with a UR-20 spectrometer. The physical constants of all of the synthesized benzoxazinonium perchlorates (melting points and IR spectra) were in agreement with those of genuine samples [1, 3].

**2-Propyl-4H-1,3-benzoxazin-4-onium Perchlorate (V,  $\text{R} = \text{C}_3\text{H}_7$ ).** A 1-ml sample of 70% perchloric acid was added to a mixture of 1.19 g (0.01 mole) of salicylnitrile in 10 ml of butyric anhydride, and the mixture was then heated to the boiling point, cooled, and diluted with absolute ether. The resulting precipitate was removed by filtration and recrystallized from glacial acetic acid to give 2.31 g (80%) of a product with mp  $211^\circ$ .

Similarly, perchlorates V ( $\text{R} = \text{CH}_3$ ,  $\text{C}_2\text{H}_5$ ,  $\text{C}_4\text{H}_9$ , and  $\text{C}_5\text{H}_{11}^*$ ) were synthesized in 88, 40, 68, and 50% yields, respectively, by acylation of salicylnitrile with acetic, propionic, valeric, and caproic anhydrides.

**2-Methyl-4H-1,3-benzoxazin-4-onium Perchlorate (V,  $\text{R} = \text{CH}_3$ ).** A mixture of 1.19 g (0.01 mole) of salicylnitrile, 2.60 g (0.01 mole) of tin perchlorate, and 15 ml of glacial acetic acid was refluxed for 3 h, after which it was cooled, 1 ml of 70% perchloric acid was added, and the mixture was diluted with ether. Workup gave 0.71 g (27%) of a product with mp  $208^\circ$  (from glacial acetic acid).

Perchlorate V ( $\text{R} = \text{C}_2\text{H}_5$ ) was similarly synthesized in 26% yield.

\* This compound had mp  $103\text{--}106^\circ$  (it was reprecipitated from glacial acetic acid solution by the addition of absolute ether).

B) A mixture of 1.19 g of salicylnitrile, 1.40 g (0.01 mole) of benzoyl chloride, and 2.60 g (0.01 mole) of tin perchlorate was refluxed in 15 ml of glacial acetic acid for 2 h. after which it was cooled, 1 ml of 70% perchloric acid was added, and the mixture was diluted with ether. Workup gave 1.5 g (58%) of a product with mp 208°.

Perchlorate V ( $R = C_2H_5$ ) was similarly synthesized in 52% yield from salicylnitrile, acetyl chloride, tin perchlorate, and propionic acid.

2-Ethyl-4H-1,3-benzoxazin-4-onium Perchlorate (V,  $R = C_2H_5$ ). A 2.60-g (0.01 mole) sample of tin perchlorate was added to a solution of 1.19 g (0.01 mole) of salicylnitrile and 0.93 g (0.01 mole) of propionyl chloride in 15 ml of propionic acid, after which the mixture was refluxed for 2 h. It was then cooled, 1 ml of 70% perchloric acid was added, and the mixture was diluted with ether. Workup gave 1.65 g (60%) of the salt with mp 183-185° (from glacial acetic acid).

Perchlorate V ( $R = CH_3$ ) was similarly synthesized in 65% yield by refluxing salicylnitrile, acetyl chloride, and tin perchlorate in glacial acetic acid.

2-Butyl-4H-1,3-benzoxazin-4-onium Perchlorate (V,  $R = C_4H_9$ ). A 1-ml sample of 70% perchloric acid was added slowly dropwise to a solution of 1.37 g (0.01 mole) of salicylaldoxime in 12 ml of valeric anhydride, after which the mixture was heated to the boiling point, cooled, and diluted with ether to give 2.60 g (86%) of the salt with mp 212-214° (from glacial acetic acid).

Perchlorate V ( $R = CH_3$ ) was similarly synthesized in 95% yield.

2-Phenyl-4H-1,3-benzoxazin-4-onium Perchlorate (V,  $R = C_6H_5$ ). A 1.30-g (0.005 mole) sample of tin perchlorate was added with stirring to a mixture of 1.19 g (0.01 mole) of salicylnitrile and 0.70 g (0.005 mole) of benzoyl chloride in 10 ml of dry chloroform, after which the mixture was stirred for 20 min, and the resulting precipitate was removed by filtration and washed with absolute ether to give 1.35 g (70%) of a salt with mp 190-196° (dec.). IR spectrum: 1731, 1629, 1597, 1553, and 1505  $cm^{-1}$ . Found: C 42.6; H 3.0; Cl 26.8; N 3.1; Sn 15.8%.  $C_{14}H_{10}NO_2 \cdot \frac{1}{2}SnCl_6$ . Calculated: C 43.1; H 2.6; Cl 27.3; N 3.6; Sn 15.2%. Hexachlorostannate V was suspended in glacial acetic acid. equimolar amounts of 70% perchloric acid were added, and the mixture was heated until the solid materials had dissolved completely. The solution was cooled and diluted with ether, and the resulting perchlorate was crystallized from glacial acetic acid-nitromethane to give a product with mp 247°.

Perchlorate V ( $R = CH_3$ ) was similarly obtained in 24% yield.

2-Phenyl-4H-1,3-benzoxazin-4-one (VI,  $R = C_6H_5$ ). This compound was obtained by the method in [3] by treatment of the appropriate hexachlorostannate with an equimolar amount of anhydrous freshly distilled triethylamine. Workup gave a product with mp 100-102° (from cyclohexane) [7] in 40% yield.

#### LITERATURE CITED

1. G. N. Dorofeenko, Yu. I. Ryabukhin, and V. V. Mezheritskii, *Zh. Org. Khim.*, **10**, 2233 (1974).
2. H. Meerwein, P. Laasch, R. Mersch, and J. Spille, *Ber.*, **89**, 209 (1956).
3. Yu. I. Ryabukhin, G. N. Dorofeenko, and V. V. Mezheritskii, *Khim. Geterotsikl. Soedin.*, No. 4, 460 (1975).
4. E. N. Zil'berman, E. N. Mizinov, S. M. Danov, R. V. Efremov, and O. P. Drachkova, *Zh. Org. Khim.*, **10**, 197 (1974).
5. L. Field, P. B. Hughmark, Shumaker, and W. S. Marshall, *J. Am. Chem. Soc.*, **83**, 1983 (1961).
6. E. Beckmann, *Ber.*, **26**, 2621 (1893).
7. G. Kollezh, T. Kappe, and E. Ziegler, *Monatsh.*, **99**, 2167 (1968).