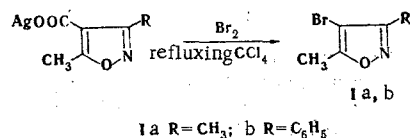


# BORODIN - HUNSDIECKER REACTION IN THE ISOXAZOLE SERIES

S. D. Sokolov and T. N. Egorova

UDC 547.786:542.944.9

The homolytic substitution of hydrogen in an isoxazole ring has not yet been described. We have found that the silver salts of isoxazole-4-carboxylic acids react smoothly with bromine and form 4-bromoisoxazoles via the scheme of the Borodin-Hunsdiecker reaction, for which a free-radical chain mechanism for decomposition of the intermediate acyl hypobromite has been established.



This method was used to obtain 3,5-dimethyl-4-bromoisoxazole (Ia) with bp 62-64° (15 mm) and  $n_D^{20}$  1.4891 [1] in 47% yield; no melting-point depression was observed for a mixture of the 2,3,5-trimethyl-4-bromoisoxazolium chloroferrates obtained from this product and a genuine sample. 3-Phenyl-4-bromo-5-methylisoxazole (Ib) with bp 128-130° (5 mm) and  $n_D^{20}$  1.5816, was similarly obtained. Found: Br 33.4%. C<sub>10</sub>H<sub>8</sub>BrNO. Calculated: Br 33.6%.

Isoxazole-3- and isoxazole-5-carboxylic acids give mixtures of products with predominance of acyclic compounds. 5-Phenylisoxazole-3-carboxylic acid gave 3-bromo-5-phenylisoxazole in ~10% yield (the PMR spectrum of a CCl<sub>4</sub> solution has a singlet at 6.48 ppm). Thus 4-isoxazolyl radicals are more stable than 3-isoxazolyl radicals.

## LITERATURE CITED

1. A. Quilico and R. Justoni, Rend. Ist. Lombardo Sci., Pt. 1, 69, 587 (1936); Chem. Zentralblatt, 1, 1424 (1937).

S. Ordzhonikidze All-Union Scientific-Research Pharmaceutical-Chemistry Institute, Moscow. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 12, pp. 1697-1698, December, 1974. Original article submitted June 17, 1974.

©1976 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 \$15.00.