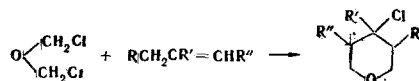


NEW METHOD FOR THE PREPARATION OF
TETRAHYDROPYRAN DERIVATIVES

A. A. Gevorkyan, Sh. O. Badanyan,
and A. A. Manukyan

UDC 547.811

In a study of the reaction of bis(α -chloroalkyl) ethers with a number of monoolefins in the presence of zinc chloride and copper chloride, we detected a new reaction leading to the formation of tetrahydropyran derivatives according to the following general scheme:



The structures of the pyrans obtained were proved by the results of IR spectroscopy and elementary analysis, as well as by alternative synthesis. Thus the reaction of 1,3-dichloro-2-butene with bis(α -chloromethyl) ether gave 3-(chloromethyl)-4,4-dichlorotetrahydropyran that was identical to that reported in [1].

The tetrahydropyrans listed below were prepared by the new method.

EXPERIMENTAL

3-Propyl-4-chlorotetrahydropyran. This was obtained in 40% yield and had bp 91° (16 mm), d_4^{20} 1.0398, and n_D^{20} 1.4630. Found %: Cl 22.38. $C_8H_{15}ClO$. Calculated %: Cl 21.80.

3,5-Trimethylene-4-chlorotetrahydropyran. This was obtained in 45% yield and had bp 85° (7 mm), d_4^{20} 1.1296, and n_D^{20} 1.4960. Found %: C 58.70; H 8.0; Cl 21.30. $C_8H_{13}ClO$. Calculated %: C 59.80; H 8.0; Cl 22.1.

3-Methyl-4,4-dichlorotetrahydropyran. This was obtained in 35% yield and had bp 54-55° (4 mm), d_4^{20} 1.3674, and n_D^{20} 1.4655. Found %: C 42.50; H 6.09; Cl 41.25. $C_6H_{10}Cl_2O$. Calculated %: C 42.60; H 5.91; Cl 42.01.

4-Methyl-4-chlorotetrahydropyran. This was obtained in 25% yield and had bp 44-45° (12 mm), d_4^{20} 1.0547, and n_D^{20} 1.4480. Found %: C 53.60; H 8.10. $C_6H_{11}ClO$. Calculated %: C 53.53; H 8.17.

3-Chloromethyl-4,4-dichlorotetrahydropyran. This was obtained in 50% yield and had bp 104° (13 mm), d_4^{20} 1.378, and n_D^{20} 1.5050. According to [1], I has bp 104° (13 mm), d_4^{20} 1.390, and n_D^{20} 1.5040. The identical character of the samples obtained by the two methods was proved by gas-liquid chromatography with a 2.5-m long column [1% polyethyleneglycol on Chromosorb G, column temperature 160°, gas (nitrogen) flow rate 60 ml/min].

Investigations to ascertain the dependence of the course of the reaction on the structural peculiarities of the reagents and studies of the range of application of the reaction are continuing.

LITERATURE CITED

1. S. A. Vartanyan, A. A. Gevorkyan, and F. V. Dangyan, *Izv. AN ArmSSR, Ser. Khim.*, **15**, 259 (1962).

Institute of Organic Chemistry, Academy of Sciences of the Armenian SSR, Erevan. Translated from *Khimiya Geterotsiklicheskikh Soedinenii*, No. 7, p. 997, July, 1971. Original article submitted July 23, 1970.

© 1974 Consultants Bureau, a division 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 \$15.00.