

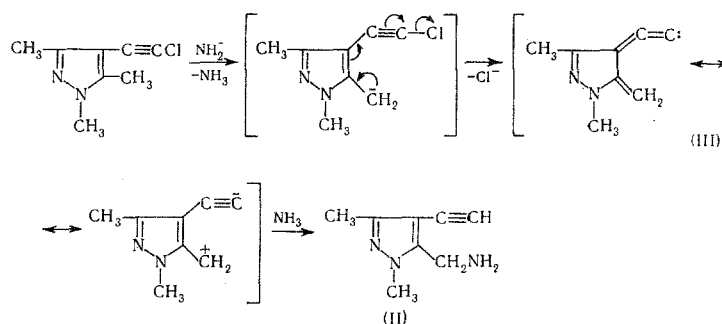
# UNUSUAL SUBSTITUTION IN PYRAZOLYLCHLOROACETYLENE SERIES

M. S. Shwartsberg and S. F. Vasilevskii

UDC 542.91:547.771:547.362

We found that the reaction of  $\text{NaNH}_2$  in liquid  $\text{NH}_3$  with 4- $\beta$ -chloroethynyl-1,3,5-trimethylpyrazole (I) [mp 83-84°. Found: Cl 21.02%.  $\text{C}_8\text{H}_9\text{N}_2\text{Cl}$ . Calculated: Cl 21.03%. Infrared spectrum in  $\text{CCl}_4$ : 2230  $\text{cm}^{-1}$  ( $\text{C}\equiv\text{C}$ ). NMR spectrum in  $\text{CCl}_4$  ( $\delta$ , ppm): 3.54 ( $\text{NCH}_3$ ), 2.10 and 2.17 (3- and 5- $\text{CH}_3$ )], obtained in 63.5% yield by the dehydrochlorination of 4- $\alpha, \beta$ -dichlorovinyl-1,3,5-trimethylpyrazole with a stoichiometric amount of the same base, unexpectedly leads to 4-ethynyl-5-aminomethyl-1,3-dimethylpyrazole (II) in 85% yield, mp 76-76.5° (from petroleum ether). Found: C 64.35; H 7.46; N 28.31%.  $\text{C}_8\text{H}_{11}\text{N}_3$ . Calculated: C 64.40; H 7.43; N 28.17%. Infrared spectrum ( $\text{CCl}_4$ ,  $\nu$ ,  $\text{cm}^{-1}$ ): 2118 ( $\text{C}\equiv\text{C}$ ), 3320 ( $\text{C}\equiv\text{CH}$ ), 3400, 3220, 1618 ( $\text{NH}_2$  assoc.). NMR spectrum ( $\text{CDCl}_3$ ,  $\delta$ , ppm): 3.79 ( $\text{NCH}_3$ ), 2.26 (3- $\text{CH}_3$ ), 3.90 ( $\text{CH}_2$ ), 1.45 ( $\text{NH}_2$ ), 3.22 ( $\text{C}\equiv\text{CH}$ ). The  $\text{CH}_3-(\text{C})$  group was identified as being 3- $\text{CH}_3$  by the character of the shifts of its signals in the NMR spectrum with change in the solvent [1].

The mechanism of the reaction was not ascertained. It is possible to postulate either a consecutive or a synchronous cleavage of a proton and chlorine anion from the methyl group and the acetylene group that is conjugated with it, and the subsequent addition of the nucleophile to the intermediate bipolar compound (III)



## LITERATURE CITED

1. J. Elgnero and R. Jacquier, *J. Chim. Phys.*, **63**, 1242 (1966).

Institute of Chemical Kinetics and Combustion, Siberian Branch of the Academy of Sciences of the USSR. Translated from *Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya*, No. 9, p. 2166, September, 1973. Original article submitted June 5, 1973.

© 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.