LETTERS TO THE EDITOR

UNUSUAL REARRANGEMENTS IN THE REACTION OF METHYLACETYLENE

WITH 1-METHYLCYCLOHEXANOYL TETRAFLUOROBORATE

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The reaction of methylacetylene (I) with 1-methylcyclohexanoyl tetrafluoroborate (II) in CH_2Cl_2 at $-60^{\circ}C$ results in the formation of ketones III and IV with a 60% yield (1:2), i.e.,



The reaction of the 2,2,6,6-d₄ analog of II with I yields the deuterated derivatives d-III and d-IV (d₄:d₃ = 61:39 in the case of d-III and d₃:d₄ = 80:20 in the case of d-IV according to the mass spectra). The presence of deuterium on the β -carbonyl carbon atom of the side chain in d-III and d-IV (PMR and mass spectra) is unequivocal evidence of the 1,5-hydride shift previously proposed for the reaction of I with cyclohexanoyl tetrafluoroborate [1].



N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR, Moscow. University of Minnesota, Duluth, U.S.A. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 3, pp. 714-715, March, 1977. Original article submitted October 18, 1976.

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 formation of III evidently takes place as a result of the constriction of the ring in intermediate B. Ketone IV can be obtained from the same intermediate B as a result of a 1,2 shift of the acyl group or by means of 1, 2 shifts of the methyl group and a hydride ion. The distribution of the deuterium shown in the following scheme (PMR spectra) is only consistent with the first mechanism (see final diagram on previous page).

The question of the migrational capacity of the acyl group in reactions of carbonium ions has scarcely been studied; however, individual examples point to the possibility that such shifts do occur (see, for example [2]). The structure of ketones III and IV has been proved by spectral methods and a reversed synthesis.

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SYNTHESIS OF AMMONIUM PEROXONITRATE

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Organic derivatives of pernitric acid HNO_4 , which are obtained, for example, according to the scheme [1]

$$CF_3OOH + N_2O_5 \rightarrow CF_3OONO_2 + HNO_3$$

are known. Inorganic derivatives of pernitric acid are unknown. We have obtained ammonium peroxonitrate NH₄NO₄ by replacing the trifluoromethyl hydroperoxide in the reaction by ammonium hydroperoxide. The synthesis was carried out by applying a solution of N₂O₅ in CCl₄ to a suspension of ammonium hydroperoxide in the same medium at -20°C in a nitrogen atmosphere with a mole ratio between the reactants equal to 0.66:1. The peroxide oxygen in the reaction product was determined permanganatometrically, the total nitrogen was determined according to Devarda's method, and the ammonium ion was determined in the form of the tetraphenylborate. The proportions found were NH₄:NO₃:O_a = 0.98:1.08:0.98 (O_a is the peroxide oxygen).

By recording the heating curves of weighed microsamples of preliminarily frozen solutions of N_2O_5 in CCl₄ with additions of ammonium hydroperoxide it was found that vigorous decomposition occurs at 5°C.

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