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SYNTHESIS OF ACETYLENIC CARBINOLS OF THE 2,2,6,6-TETRAMETHYLPIPERIDINE SERIES

V. V. Pavlikov, L. N. Skripnichenko, UDC 542.91:547.362:547.822.3

- L. A. Ustynyuk, V. V. Murav'ev,
- A. B. Shapiro, and É. G. Rozantsev

Acetylenic carbinols of the 2,2,6,6-tetramethylpiperidine series are intermediates in the synthesis of heat and light stabilizers for polymers, fuels, and lubricating oils [1-3]. They can also be used to obtain compounds for biological and medical studies [4].

However, at the present time satisfactory methods are lacking for the preparation of the ethynylcarbinol derivatives of 2,2,6,6-tetramethylpiperidine. The known methods [5, 6] have a number of serious disadvantages that makes their use difficult. In order to improve these methods, the ethynylation of 2,2,6,6-tetramethyl-4-oxopiperidine (I) was studied in the present paper under the conditions of the method given in [7], and specifically: in liquid ammonia as the medium, in the presence of 20% alcoholic KOH solution, at ~ 20° C, and a pressure of 10-18 gauge atm.



The use of this method made it possible to increase the reaction rate, exclude the use of absolute toxic solvents, and eliminate the need of strictly-maintaining low-temperature conditions for a long time. The need of using a large excess of powdered KOH is eliminated, and the sensitivity of the reaction to impurities in the starting products decreases sharply.

EXPERIMENTAL

<u>4-Hydroxy-4-ethynyl-2,2,6,6-tetramethylpiperidine (II)</u>. Into a 1-liter steel autoclave were loaded a solution of 155 g of (I) in 150 ml of EtOH, 250 ml of 20% ethanolic KOH solution, and 300 ml of liquid NH₃. Then, with cooling of the autoclave in dry ice, the reaction mixture was saturated with acetylene under a pressure of 14-18 gauge atm, after which the autoclave was allowed to stand for 5 h at ~20°. The obtained precipitate was filtered, washed with water, and dried in a vacuum desiccator. We obtained 181 g (~100%) of (II) as a white crystalline powder with mp 213° (after sublimation in vacuo). Found: C 72.85; H 10.39; N 7.76%; mol. wt. 181 (mass spectrometry). C₁₁H₁₉NO. Calculated: C 72.98; H 10.50; N 7.72%.

<u>4-Hydroxy-4-vinylethynyl-2,2,6,6-tetramethylpiperidine (III)</u>. A mixture of 155 g of (I) in 150 ml of EtOH, 250 ml of 20% ethanolic KOH solution, and 300 ml of liquid NH₃ was saturated with vinylacetylene under a pressure of 8 gauge atm, with cooling of the autoclave in dry ice, after which the autoclave was allowed to stand for 8 h at ~20°. The reaction mixture was evaporated to half volume and then diluted with a 10-fold excess of water. The obtained precipitate was filtered to give 131 g (63%) of (III) as a white crystalline powder with mp 110° (hexane). Found: C 75.38; H 10.30; N 7.05%; mol. wt. 207 (mass spectrometry). $C_{13}H_{21}NO$. Calculated: C 75.36; H 10.14; N 6.76%.

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<u>4-Hydroxy-4-phenylethynyl-2,2,6,6-tetramethylpiperidine (IV)</u>. A mixture of 155 g of (I) in 150 ml of EtOH, 250 ml of 20% ethanolic KOH solution, 102 g of phenylacetylene, and 300 ml of liquid NH₃ was kept in an autoclave for 8 h at ~20°. After the same workup as in the synthesis of (III), we obtained 146 g (56.8%) of (IV) as a white crystalline powder with mp 108° (hexane). Found: C 79.35; H 8.87; N 5.31%; mol. wt. 257 (mass spectrometry). $C_{17}H_{23}NO$. Calculated: C 79.38; H 8.95; N 5.45%.

CONCLUSIONS

A convenient method was proposed for the preparation of acetylenic carbinols of the 2,2,6,6-tetramethylpiperidine series by the ethynylation of 2,2,6,6-tetramethyl-4-oxopiperidine in liquid ammonia in the presence of alcoholic alkali.

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REDUCTION OF PERFLUOROCARBOXYLIC ACID

ANHYDRIDES TO 1,1-DIHYDROPERFLUORO

ALCOHOLS

G. D. Kolomnikova, M. I. Kalinkin, Z. Ts. Tskhurbaeva, Z. N. Parnes, and D. N. Kursanov UDC 542.941:547.464-312

1,1,-Dihydroperfluoro alcohols are usually obtained by the reduction of perfluorocarboxylic acids or their derivatives with aluminum lithium hydride [1]. Methods for the catalytic hydrogenation of perfluorocarboxylic acid derivatives have received little study. Trifluoroacetic anhydride [2] and trifluoroacetamide [3] are hydrogenated to trifluoroethanol on Adams catalyst. Copper chromite catalyzes the hydrogenation of perfluorocarboxylic esters to the corresponding alcohols at 210°C and a pressure of 250 atm [4].

Recently it was proposed [5] to use trimethylsilane for the reduction of perfluoro acid fluorides in the presence of Pt/C, $ZnCl_2$, and KF. The reaction is run in an autoclave at 160-210°, and the yield of the formed esters or lactones in the case of dibasic acids is 10-30%. The drastic conditions of the last reaction can be explained by the absence of a sufficiently strong electrophilic agent in the reaction sphere, which activates the carbonyl group for reaction with the silane.

We found that perfluorocarboxylic anhydrides are easily reduced by organohydrosilanes in the presence of the corresponding acids (Table 1). The reaction proceeds under mild conditions, is preparatively simple, and leads to a mixture of the alcohol and its ester with the starting acid. The triethyl- and diphenylsilanes give comparable results in the reduction of the perfluoro anhydrides.

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