

REDUCTIVE N-ALKYLATION OF
2,5-DIMETHYL-4-TRIPHENYLSILYLPYRIDINE
OVER METAL SULFIDES

M. A. Ryashentseva, A. V. Varlamov,
N. S. Prostakov, and Kh. M. Minachev

UDC 542.941.7:66.095.253:547.82

The selective hydrogenation of the pyridine ring in polynuclear aromatic systems to the piperidine ring is important not only from the theoretical, but also from the preparative standpoint, since aryl-substituted piperidines, which are either potential physiologically active compounds or the starting substances for their synthesis, can be obtained by this route in quantitative yield. In order to study whether selective hydrogenation of the pyridine ring can be effected we employed the recently obtained 2,5-dimethyl-4-triphenylsilylpyridine (I) [1] as the model compound.

Information is absent in the literature on the behavior of organosilicon compounds in a H_2 atmosphere at high temperatures and pressure in the presence of sulfide catalysts. It is only known that tetraorganosilanes undergo hydrogenolysis at 350–490° in the presence of H_2 [2, 3]. Previously it was established that reductive N-alkylation is the main reaction in the presence of Re_2S_7 and ethanol during the hydrogenation of pyridine [4], picolines and lutidines [5], 3-methyl-2-azofluorene, 3-methyl-2-azofluorenone, and 3-methyl-9-phenyl-2-azo-9-fluorene [6]. Only the pyridine ring undergoes reduction in the azofluorenes.

Reductive N-alkylation of the pyridine ring, without involving the phenyl radicals attached to silicon, occurs when (I) is hydrogenated in ethanol in the presence of 10% of Re_2S_7 when based on the weight of (I) (270°, 6 h, or 3 h at 300°; initial H_2 pressure, 140 atm). Here hydrogenolysis and other side reactions fail to take place, and a mixture of two geometric isomers of 2,5-dimethyl-1-ethyl-4-triphenylsilylpiperidine (II) is formed in a ratio ~3:1 in quantitative yield. The Pt and Pd sulfides are less active than Re_2S_7 . Employing the method of differential-thermal analysis (DTA) [4], it was established that H_2S is formed on the Re_2S_7 surface in the presence of H_2 , and the specific action of Re_2S_7 and its high activity in the reaction for the hydrogenation of the pyridine ring is evidently associated with this. In the presence of acid centers on the catalyst surface it is possible for them to react with the nitrogen of the pyridine ring, thus leading to the formation of intermediate pyridinium complexes, which are easily hydrogenated. It is known that it is the salts, rather than the pyridine bases themselves, that are hydrogenated more easily [7, 8].

It is possible that the specific action of Re_2S_7 , when compared with that of the Pt and Pd sulfides, is associated with the fact that rhenium, in contrast to Pt and Pd, can be present in the sulfides in the 4+ and 2+ states [9].

EXPERIMENTAL METHOD

The experiments were run in an autoclave as described in [10]; the information on the catalysts is also given there. The isolated (II) isomers were characterized by the elemental analysis, and by the IR and NMR spectra. The IR spectra were obtained on the UR-20 instrument as Nujol mulls, while the NMR spectra were obtained on a HA-100D spectrometer in CCl_4 solution, using TMS as the standard.

Into the autoclave were charged 6 g of (I), 0.6 g of rhenium heptasulfide, and 50 ml of absolute alcohol. The reaction time was 3 h, the temperature was 300°, and the initial H_2 pressure was 140 atm.

N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR. P. Lumumba University of International Friendship. Translated from *Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya*, No. 8, pp. 1901–1902, August, 1973. Original article submitted January 15, 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.

After cooling the reaction mass the catalyst was filtered and washed repeatedly with alcohol. The alcohol was distilled off, and the residue (5.87 g) was separated on a column (23 × 760 mm) packed with Al₂O₃ (II activity), using an ethyl acetate–hexane mixture (1:15 by volume) for elution. We isolated: a) 0.78 g of the (II) isomer with R_f 0.56 (Al₂O₃, II activity, 1:3 ethyl acetate–hexane). Infrared spectrum (ν , cm⁻¹): 2796 s (NC₂H₅), 1587 w (aromatic C=C bonds), 1425 s and 1108 v. s. (SiC₆H₅). NMR spectrum (δ , ppm): 2.25 (CH₂ quartet in NC₂H₅), 0.72–1.00 (multiplet, 9H, CH₃ groups). Hydrochloride, mp 244–245° (ethyl acetate–acetone). Found: C 74.1; H 8.3; N 3.3; Cl 8.3; Si 6.2%. C₂₇H₃₄NSi·HCl. Calculated: C 74.4; H 7.8; N 3.2; Cl 8.2; Si 6.4%. Picrate, mp 193.5–195° (alcohol–acetone). Found: N 9.5%. C₂₇H₃₃NSi·C₆H₃N₃O₇. Calculated: N 9.3%; b) 2.3 g of the (II) isomer with R_f 0.46. Infrared spectrum (ν , cm⁻¹): 2790 s (NC₂H₅), 1591 w (aromatic C=C bonds), 1428 and 1110 v. s. (SiC₆H₅).

Hydrochloride, mp 198.5–200° (ethyl acetate–acetone). Found: C 74.1; H 8.2; N 3.1; Cl 7.9; Si 6.8%. C₂₇H₃₃NSi·HCl. Calculated: C 74.4; H 7.8; N 3.2; Cl 8.2; Si 6.4%. Picrate, mp 182–183.5° (alcohol–acetone). Found: N 9.2%. C₂₇H₃₃NSi·C₆H₃N₃O₇. Calculated: N 9.3%. In addition, we isolated 2.5 g of mixed (II) isomers.

CONCLUSIONS

The Re₂S₇ catalyst was proposed, and optimum conditions were established, for the selective hydrogenation of the pyridine ring in 2,5-dimethyl-4-triphenylsilylpyridine and its subsequent N-ethylation with ethanol, without involving the phenyl radicals attached to silicon. The Pt and Pd sulfides are less active under analogous conditions.

LITERATURE CITED

1. N. S. Prostakov and A. V. Varlamov, *Khim. Geterotsikl. Soed.*, **6**, 1637 (1970).
2. V. N. Ipat'ev and B. N. Dolgov, *Zh. Obshch. Khim.*, **1**, 5 (1931).
3. B. N. Dolgov and Yu. N. Vol'nov, *Zh. Obshch. Khim.*, **1**, 91 (1931).
4. M. A. Ryashentseva, Kh. M. Minachev, and N. Tsibizova, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1583 (1973).
5. M. A. Ryashentseva, E. A. Mistryukov, and E. L. Il'kova, Author's Certificate No. 293805 (January 23, 1970); *Byull. Izobr.*, No. 6, 61 (1971); E. A. Mistryukov, E. L. Il'kova, and M. A. Ryashentseva, *Tetrahedron Lett.*, 1691 (1971).
6. M. A. Ryashentseva, Kh. M. Minachev, N. S. Prostakov, G. Al'vorado-Urbina, and L. A. Gai-varonskaya, Author's Certificate No. 327193 (July 11, 1970); *Byull. Izobr.*, No. 5, 68 (1972).
7. O. Wibaut, *Rec. Trav. Chim.*, **50**, 957 (1931).
8. H. Adams, *J. Amer. Chem. Soc.*, **50**, 2260 (1928).
9. W. H. Davenport, V. Kollonitsch, and C. H. Kline, *Ind. Eng. Chem.*, **60**, 11 (1968).
10. M. A. Ryashentseva, Kh. M. Minachev, V. V. Dorogov, and N. S. Prostakov, *Khim. Geterotsikl. Soed.*, **7**, 88 (1972).