

This article was downloaded by:

On: 27 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Organic Preparations and Procedures International

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t902189982>

CONVENIENT SYNTHESIS OF 2-TRIMETHYLSILYLOXYPYRIDINES

M. V. Prostenik^a

^a Pharmaceutical and Chemical Works, PLIVA, Zagreb, Croatia YUGOSLAVIA

To cite this Article Prostenik, M. V. (1979) 'CONVENIENT SYNTHESIS OF 2-TRIMETHYLSILYLOXYPYRIDINES', *Organic Preparations and Procedures International*, 11: 5, 251 – 253

To link to this Article: DOI: 10.1080/00304947909354855

URL: <http://dx.doi.org/10.1080/00304947909354855>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

by working under N_2 with oven-dried glassware. The structure proof for II is based primarily on its spectral properties.

IR (CCl_4) cm^{-1} : 3000 and 2950 (CH stretch), 1600 (C=N stretch), 1460 (sh), 1440-1420, 1380, 1360, 1340, 1250, 1190, 1140, 1100, 1040; MS (m/e): 87.0687 (P, 100%, calc. 87.0684), 72.0445 (P-Me, 25%, Calc. 72.0449), 71 (P-O, 25%), 59 (P-C₂H₄, 60%), 56 (P-Me-O, 60%); ¹H NMR (CDCl₃-TMS) δ : 1.40 (t, 3H, J = 7 Hz), 1.95 (d, 3H, J = 6 Hz), 3.85 (q, 2H, J = 7 Hz), 7.10 (q, 1H, J = 6 Hz); ¹³C NMR (CDCl₃) ppm: 10.5 (methyl), 11.3 (methyl), 57.6 (CH₂, J_{13CH₃} = 141 Hz), 132.0 (vinyl CH, J_{13CH} = 179 Hz).

REFERENCES

- † Tata Institute of Fundamental Research, Homi Bhabha Road, Bombay 400 005, India
1. T. Caceres, E. Lissi and E. Sanhueza, *Int. J. Chem. Kinetics*, **10**, 1167 (1978).
 2. D. Schaal, K. Partymiller and J. Heicklen, *Science Total Environ.*, **2**, 209 (1978) and references therein.
 3. E. G. Rozantsev, "Free Nitroxyl Radicals," *Eng. trans. by B. J. Hazzard*, p. 208, Plenum, New York, N. Y., 1970.

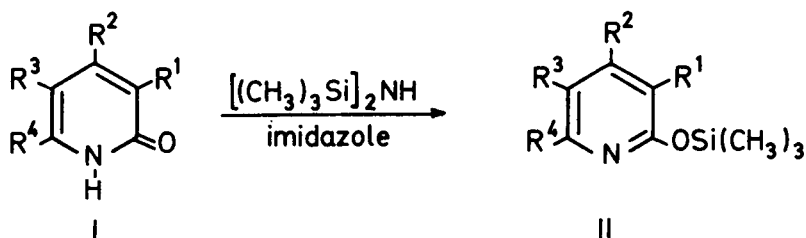
CONVENIENT SYNTHESIS OF 2-TRIMETHYLSILYLOXYPYRIDINES

Submitted by M. V. Prostenik
(6/21/78)

PLIVA, Pharmaceutical and Chemical Works
41000 Zagreb, Croatia, YUGOSLAVIA

Hexamethyldisilazane is an efficient derivatizing agent for use in the gas chromatographic analysis of relatively non-volatile 2-(1H)-pyridones. Excellent yields of 2-trimethylsilyloxy pyridines II were obtained in six cases examined (Table 1), by treatment of I with hexamethyldisilazane in

the presence of imidazole.¹



The products were isolated by distillation in vacuo. All silyl enolates (II) exhibited characteristic IR absorptions at 1600, 1250, 1150 and 850 cm^{-1} . The spectra lacked the NH hydrogen bonded absorptions at 3100-2500 cm^{-1} of the parent 2-(1H)-pyridones I.

EXPERIMENTAL

IR spectra were recorded on a Perkin-Elmer Model 257 spectrophotometer as films. Gas-liquid chromatography was performed on Perkin-Elmer Model F-11 using: 2m x 3mm column, 3% SF-96 on 80-100 mesh Chromosorb G-AW-DMCS, flame ionization detector, nitrogen (30 ml/min) as carrier gas, column temperature 140°C. Starting pyridones Ia and If were commercial products (Aldrich), while pyridones Ib, Ic, Id, and Ie were prepared by published procedures.^{2,3}

Table 1. 2-Trimethylsilyloxy pyridines II

Cpd. No	R ¹	R ²	R ³	R ⁴	bp. °C (mm)	Yield %	Anal.	
							Calcd. C	(Found) H
IIa	CN	CH ₃	H	CH ₃	157 (20)	93.6	59.95 (60.11)	7.33 (7.37)
IIb	CN	CH ₃	Cl	CH ₃	149 (18)	92.5	51.85 (51.56)	5.95 (5.96)
IIc	CN	CH ₂ OMe	H	CH ₃	157 (18)	97.1	57.56 (57.63)	7.26 (7.11)
II d	CN	CH ₃	H	CH ₂ OMe	108 (0.4)	94.4	57.56 (57.30)	7.26 (7.02)
IIe	H	CH ₃	H	H	81 (18)	92.4	59.62 (59.39)	8.33 (8.07)
II f	H	H	H	CH ₃	72 (18)	89.3	59.62 (59.84)	8.33 (8.15)

Silylation of 2-(1H)-pyridone. General Procedure.- Pyridones I (0.015 mol), imidazole (0.06 g., 0.09 mol) and hexamethyldisilazane (15 g., 0.09 ml) were stirred at 70° for 1.5 hr. After removal of excess hexamethyldisilazane at 150 mmHg, the remaining crude products were fractionated in vacuo (see Table 1) to give 2-trimethylsilyloxy pyridines II as colorless liquids. All these compounds are extremely sensitive to moisture.

REFERENCES

1. R. S. Glass, *J. Organometal. Chem.*, 1973, 83; S. Torkelson and C. Ainsworth, *Synthesis*, 1976, 722.
2. M. V. Prostenik, V. Slukan, F. Zorko, Z. Hranilovic and S. Skreb, *Croat. Chem. Acta*, 48, 179 (1976); *CA*, 85, 108492f (1976).
3. M. V. Balykina, E. S. Zhdanovich and N. A. Preobrazenskii, *Tr. Vses. Nauchn. - Issled. Vitamin Inst.*, 7, 8 (1961); *CA*, 59, 11417 (1963).

SIMULTANEOUS PREPARATION OF BROMOACETIC ACID AND ACETYL CHLORIDE

Submitted by Janusz Swietoslowski
(12/26/78)

The Research Laboratory of the "Organika-Azot"
Works, 32-510 Jaworzno, POLAND

Aleksander Ratajczak*

Department of Organic Synthesis, Silesian
University, 40-006 Katowice, POLAND

The successful use of bromine chloride as a bromination agent has been reported for bromination of arene rings¹⁻⁴ and preparation of bromosilane derivatives.⁴ Bromination of other organic compounds has not been investigated, owing to supposed side-reactions, especially chlorination since bromine chloride in both liquid and gaseous states always occurs in equilibrium with chlorine and bromine.⁵ We now report that bromine chloride reacts easily with acetic anhydride. The reaction proceeds very rapid-