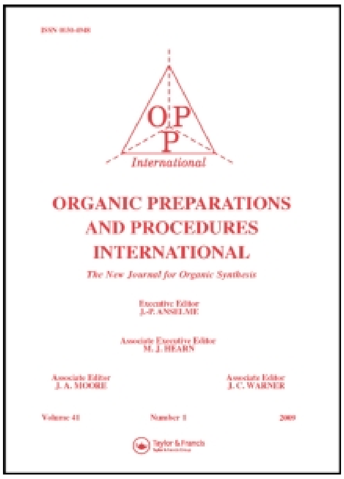

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CONVENIENT SYNTHESIS OF 2-TRIMETHYLSILYLOXYPYRIDINES

M. V. Prostenik[a]
[a] Pharmaceutical and Chemical Works, PLIVA, Zagreb, Croatia YUGOSLAVIA

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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 ($P-C_2H_4$, 60%), 56 (P-Me-O, 60%); ^1H NMR ($CDCl_3$-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); ^{13}C NMR ($CDCl_3$) ppm: 10.5 (methyl), 11.3 (methyl), 57.6 (CH_2, $J_{^{13}CH_3}$ = 141 Hz), 132.0 (vinyl CH, $J_{^{13}CH}$ = 179 Hz).

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† Tata Institute of Fundamental Research, Homi Bhabha Road, Bombay 400 005, India

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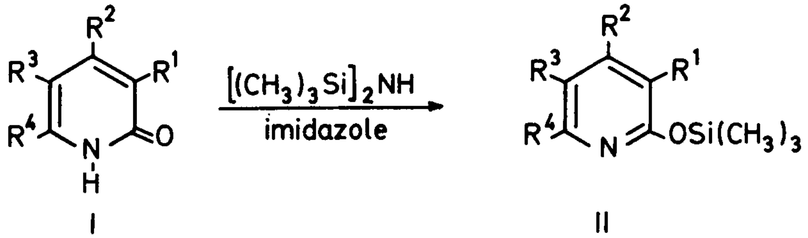
CONVENIENT SYNTHESIS OF 2-TRIMETHYLSILYLOXYPYRIDINES

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-trimethylsilyloxypyridines 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. (Found) C	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_2OMe	H	CH_3	157 (18)	97.1	57.56 (57.63)	7.26 (7.11)
IId	CN	CH_3	H	CH_2OMe	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)
IIf	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.

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SIMULTANEOUS PREPARATION OF BROMOACETIC ACID AND ACETYL CHLORIDE

Submitted (12/26/78)

by Janusz Swietoslawski

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 rings[1-4] 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-