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IPSO SUBSTITUTION OF HETEROCYCLIC TRIMETHYLSILYL CARBOXYLATES BY CARBON ELECTROPHILES [1,#]

FRANZ EFFENBERGER* and JOACHIM KÖNIG [2]

Institute for Organic Chemistry, University of Stuttgart,
Pfaffenwaldring 55, D-7000 Stuttgart 80,
Federal Republic of Germany

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Summary: Trimethylsilyl esters 1 of heterocyclic carboxylic acids having the ester group in the α-position to an azine nitrogen atom react with aldehydes or ketones through ipso substitution of the ester group to give (trimethylsiloxy)-alkyl-substituted heterocyclic products in good yields.

Electrophilic substitution of heterocyclic compounds having an azine nitrogen is only possible in exceptional cases as a result of the strong interaction between the electrophile and the basic nitrogen atom. In contrast, the corresponding N-oxides generally react with both nucleophiles and electrophiles to furnish substitution or addition products in good yields.[3] A further possibility for electrophilic substitution of heterocycles with azine nitrogen atoms is the ipso substitution of the corresponding trimethylsilyl (TMS)-substituted compounds.[4] A disadvantage of this reaction, however, is the fact that some of the required heterocycles are only difficultly accessible[5] and must often be prepared by silylation of organometallic compounds.

We have observed the formation of 2-trimethylsilylpyridine on heating trimethylsilyl 2-pyridinecarboxylate(1a).[6] Since heterocyclic carboxylic acids are usually easily accessible by the oxidation of alkyl-substituted heterocycles, we have investigated the pyrolysis of other heterocyclic trimethylsilyl carboxylates as a possible method for the preparation of TMS-substituted heterocycles. However, only in the case of the conversion of 1a to 2-trimethylsilylpyridine we were able to obtain a maximal yield of 40%; the pyrolyses of other heterocyclic trimethylsilyl carboxylates gave markedly lower yields of the TMS-substituted heterocycles. Thus, the method is not suitable for the preparation of TMS-substituted heterocycles.

It is highly probable that the pyrolysis of heterocyclic trimethylsilyl carboxylates proceeds through hetaryl anions,[7] which are known to be the decisive intermediates in base-catalyzed carbodesilylations.[4a] It thus seemed worthwhile to perform the pyrolysis of heterocyclic trimethylsilyl carboxylates in the presence of electophiles which should then react directly with the anionic intermediates formed *in situ*.

Hammick et al.[8] have investigated the decarboxylation of heterocyclic carboxylic acids in the presence of carbon electrophiles and, in many cases, have found that decarboxylation occurs with simultaneous introduction of the electrophile at the ipso-position (Hammick reaction). Although the Hammick reaction can be employed with a wide range of heterocyclic carboxylic acids, many examples are also known where the reaction fails completely, such as with 4-pyrimidine- and 2-thiazolecarboxylic acids,[9a] or where it gives rise to very poor product yields, such as with 2-pyrimidinecarboxylic acid N-oxide[9b] or 3-pyridazinecarboxylic acid.[9c]

Dedicated to Professor Edward C. Taylor on the occasion of his 65th birthday.

Pyrolysis of Trimethylsilyl 2-Pyridinecarboxylate (1a) in the Presence of Aldehydes or Ketones

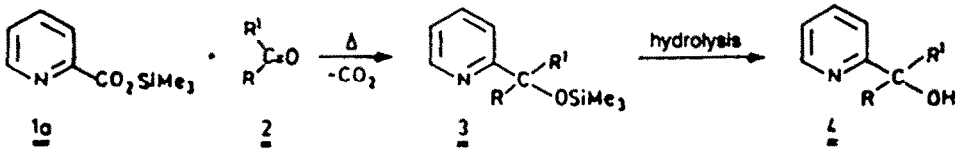
Heterocyclic trimethylsilyl carboxylates can be prepared simply and in very good yields from heterocyclic carboxylic acids and 1,1,1,3,3,3-hexamethyldisilazane (HMDS) (see experimental section). For the example of the reaction of 1a with differing carbon electrophiles 2 (aldehydes, ketones, carboxylic acid chlorides), we have examined the range of variability of the carbon electrophile and have also optimized the reaction conditions. Since cleavage of CO_2 begins only at temperatures of 180 °C or more, we have only allowed carbonyl compounds 2 with correspondingly high boiling points to react with 1a in the absence of a solvent. In this manner we have employed aromatic and aliphatic aldehydes and obtained the carbodecarboxylation products 3 in very good yields; the aliphatic aldehyde 2c reacted faster than the aromatic aldehydes 2a,b. In contrast, the reaction with benzophenone (2e) took place much more slowly. When 1a and benzoyl chloride were heated, methyltrichlorosilane was cleaved (isolated in 57% yield) and a resinous product was formed.

It is known that the rates of many desilylation reactions are accelerated by the presence of nucleophiles such as, e.g., fluorides.[4a] However, from the reaction of 1a with 2b in the presence of a molar amount of cesium fluoride even at 60-70 °C, we obtained only fluorotrimethylsilane and cesium 2-pyridinecarboxylate; in the presence of catalytic amounts of cesium fluoride the reaction was less clear than the uncatalyzed reaction and gave rise to more by-products. We therefore performed all further reactions without the addition of a catalyst.

Compounds 3 can be hydrolyzed to the alcohols 4 in practically quantitative yields by ethanol and catalytic amounts of pyridinium trifluoroacetate (see experimental section).

Table I

Pyrolysis of Trimethylsilyl 2-Pyridinecarboxylate (1a) to 2-(Trimethylsiloxyalkyl)-pyridines 3 in the Presence of Aldehydes or Ketones.



1a 2 3 4

Electrophile 2[a] R	R[1]	Reaction Conditions. Time (h)	Temp. (°C)	Product ..pyridine	Yield (%)
2a H	C_6H_5	46	200	3a 2-(phenyltrimethylsiloxymethyl)-	83
2b H	4-$CH_3OC_6H_4$	2	240	3b 2-(4-methoxyphenyltrimethylsiloxymethyl)-....	73
		22	200	3b	74
2c H	n-C_9H_{19}	6	200	3c 2-(1-trimethylsiloxydecyl)-	73
2e C_6H_5	C_6H_5	180	240	3e 2-(diphenyltrimethylsiloxymethyl)-...	61

[a] Molar ratio of 1a:2 = 1:2.

The isomeric trimethylsilyl 3- and 4-pyridinecarboxylates (1b and 1c) exhibit a completely different reaction behavior towards aldehydes and ketones than 1a. No C-C coupling products were detected after heating of 1b with 2a

(68h/240°C) and of 1c with 2b (20h/240°C). Only polymeric products in addition to small amounts of pyridine, methanol, and 40-45% hexamethyldisilazane were obtained . The mechanisms of these experimental observations can be explained without difficulty (see below).

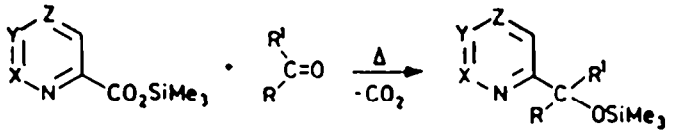
Pyrolysis of the Heterocyclic Trimethylsilyl Diazinecarboxylates 5,7, and 9 in the Presence of Aldehydes or Ketones

In analogy to the above-mentioned reactions of 1a, we have also studied the reaction behavior of the heterocyclic diazines, trimethylsilyl 2-pyrazine- (5), 3-pyrimidine- (7), and 4-pyrimidinecarboxylates (9) towards aldehydes and ketones. All three diazine derivatives reacted with aldehydes and ketones to give the corresponding substitution products 6, 8, or 10 in good to excellent yields (see Table II).

As already mentioned, the Hammick reaction gives very poor yields with 3-pyridazinecarboxylic acid and does not take place with 4-pyrimidinecarboxylic acid; no reports on the reaction with 2-pyrazinecarboxylic acid have been published. The application of the corresponding organometallic compounds in the reaction with aldehydes or ketones is often difficult or even impossible as a result of their laborious preparation and their instability. Thus, for example, 2-pyrazinyllithium can only be obtained by metallation of 2-iodopyrazine which, in turn must be obtained in a multistage synthesis; the organolithium compound cannot be obtained from 2-chloro- or 2-bromopyrazine.[11] Lithiation of pyrimidine in the 4-position cannot be achieved with pyrimidine itself or with a 4-halopyrimidine; instead 5-bromopyrimidine must be metallated with lithium diisopropylamide.[12] After completion of the reaction of the organometallic compound with the aldehyde, the bromine atom in position 5 can be cleaved hydrogenolytically.[12b] Thus, thermolysis of heterocyclic trimethylsilyl carboxylates in the presence of aldehydes or ketones represents a preparatively interesting alternative for the synthesis of trimethylsiloxyalkylsubstituted heterocycles.

Table II

Pyrolysis of Trimethylsilyl 2-Pyrazine- (5), 3-Pyridazine- (7), and 4-Pyrimidinecarboxylates (9) in the Presence of Aldehydes or Ketones 2 to give the Trimethylsiloxymethyl-Substituted Heterocyclic Diazines 6, 8, and 10.

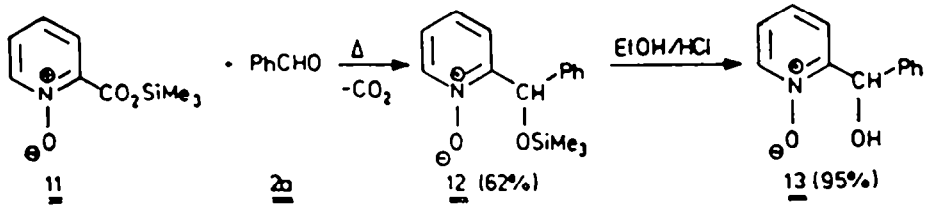


5, 7, 9 2 6, 8, 10

	Substrates[a] X	Y	Z	2	Conditions Time (h)	Temp (°C)	Product		Yield (%)
5	CH	CH	N	2a	90	200	6a	2-(phenyltrimethylsiloxymethyl)-pyrazine	50
5[b]				2b	120	200	6b	2-(4-methoxyphenyltrimethylsiloxymethyl)-pyrazine	42
5				2b	48	200	6b		52
5				2e	312	240	6e	2-(diphenyltrimethylsiloxymethyl)-pyrazine	23
7	N	CH	CH	2a	72	125	8a	3-(phenyltrimethylsiloxymethyl)-pyridazine	67
7				2b	43	150	8b	3-(4-methoxyphenyltrimethylsiloxymethyl)-pyridazine	81
7				2d[c]	144	115	8d	3-(4-chlorophenyltrimethylsiloxymethyl)-pyridazine	70
9	CH	N	CH	2a	22	180	10a	3-(phenyltrimethylsiloxymethyl)-pyrimidine	66

[a] Molar ratios of 5:2, 7:2, and 9:2 = 1:2 [b] Molar ratios of 5:2b = 1:1 [c] 4-Chlorobenzaldehyde.

Trimethylsilyl 2-pyridinecarboxylate 1-oxide (11) represents an interesting example of the reaction of heterocyclic trimethylsilyl carboxylates for the discussion of the reaction mechanism (see next Section) because the rate of decarboxylation of 2-pyridinecarboxylic acid 1-oxide is 160 times higher than that of 2-pyridinecarboxylic acid.[13] The reaction of 11 with benzaldehyde (2a) to form 2-(phenyltrimethylsiloxymethyl)-pyridine 1-oxide (12) takes place at 80°C and is completed at 120°C within 4 hours. In contrast, 1a reacts with 2a at a sufficient rate only at above 180 °C (after 10h at 180°C a 36% yield of 3a can be detected by ^{1}H NMR spectroscopy). Compound 12 is hydrolyzed to 13 by ethanol and a catalytic amount of HCl. Thus, the difference in reactivity between 1a and 11 with benzaldehyde (2a) is certainly comparable with that in the decarboxylation of 1 and 11.

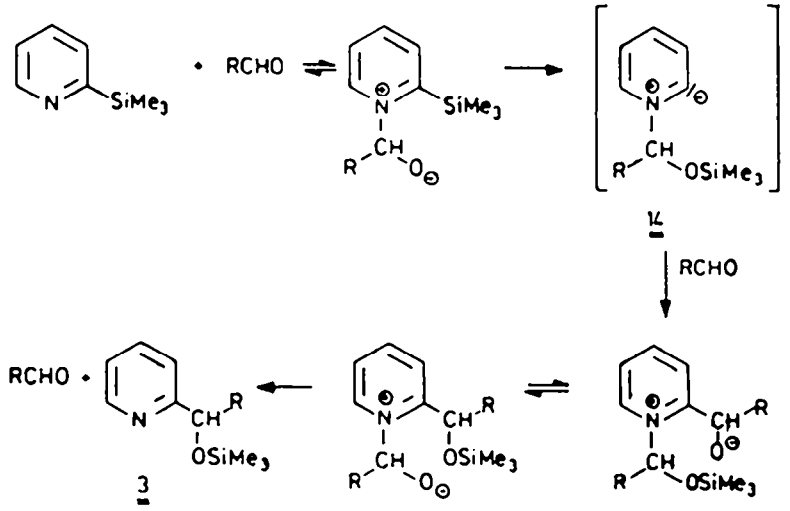


Mechanism for the Ipso Substitution of Heterocyclic Trimethylsilyl Carboxylates

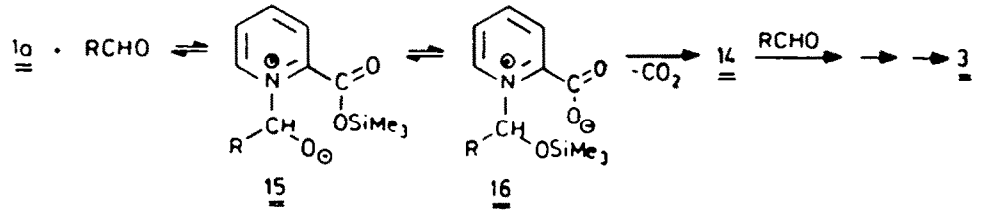
From the points of view of reaction conditions and product formation, the reactions of heterocyclic trimethylsilyl esters with carbonyl compounds are comparable on the one hand with the reactions of the corresponding heterocyclic carboxylic acids (Hammick reaction) and on the other hand with those of heterocyclic trimethylsilyl compounds.[6]

For the Hammick reaction it is assumed that the decarboxylation proceeds from the protonated form of the heterocycle (e.g. from the pyridinium salt) whereby the hetaryl anion formed is well stabilized as an ylide.[8] It has been shown for many examples that the decarboxylations of quaternary nitrogen heterocycles (N-alkylpyridinium salts, N-oxides, etc.) are considerably more rapid than those of nonquaternary compounds.[13,14] In the carbodesilylation of heterocycles with trimethylsilyl groups in the α-position to a basic nitrogen atom[6,15], an interaction is assumed to take place between the carbon electrophile and the ring nitrogen atom with subsequent detachment of the trimethylsilyl group from the quaternized intermediate to form an ylide which then reacts rapidly with the electrophile under C-C coupling.

Comparative reactions of 2-, 3-, and 4-trimethylsilyl pyridines with aldehydes have shown that the 3- and 4-isomers react well under base catalysis but not in the absence of the base,[6] whereas the 2-isomer reacts with the carbonyl compound at higher temperatures even in the absence of the base.[6,16] This result, as well as that from the decarboxylation reaction, can be explained in terms of an early equilibrium of the quaternary intermediate from 2-trimethylsilylpyridine and the carbonyl compound. This intermediate undergoes migration of the silyl group to give the ylide 14 which then reacts with further carbonyl compound through the intermediates shown in the reaction scheme to furnish the observed products.



The decarboxylation of 1a to 2-trimethylsilylpyridine mentioned at the beginning only proceeds at a sufficient rate at 240°C. In the presence of an aldehyde or ketone, CO_2 cleavage from 1a occurs at a considerably lower temperature. We therefore assume that an initial addition of the carbonyl compound to 1a also takes place here to give 15 which, as a result of the higher basicity of an alkoxide in comparison with a carboxylate as well as the favorable steric situation, undergoes silyl group migration to form 16 particularly readily. After cleavage of CO_2 the ylide 14 formed reacts with further carbonyl compound to yield the 2-trimethylsiloxyalkyl-substituted pyridine 3 as described above.



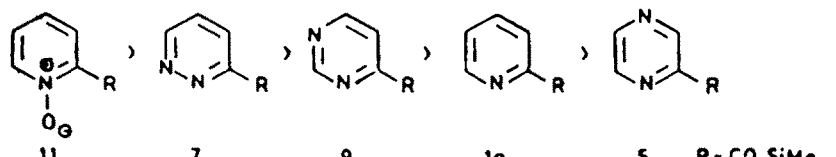
Comparative studies have shown that the rate of reaction increases not only as expected with increasing concentration of the carbonyl compound but also with increasing carbonyl activity and depends as well to a great extent on the basicity of the heterocycle. Increasing basicity increases the rate of reaction and this can be explained by a preference for adduct formation in the early equilibrium. In addition, anion stabilization at the position adjacent to the azine nitrogen atom is also of significance (the pK_a values of the corresponding carboxylic acids as well as the basic H/D exchange rates can be taken as measures for this).

Table III

Comparative Carbodesilylations of Heterocyclic Trimethylsilyl Carboxylates with Aldehydes 2 (Molar Ratio 1:2, Reaction Time 10 h)

Substrate	pk_a of the corresponding acids	-log K of the basic H/D exchanges rates	2	Temp. (°C)	Products (%, determined by ^{1}H NMR)				
1a	4.12[17]	6.7[18]	2a	180	1a	(68)	+	3a	(36)
1a			2b	180	1a	(61)	+	3b	(37)
1a			2c	180	1a	(<5)	+	3c	(70)
5	2.92[19]	5.0[18]	2a	180	5	(70)	+	6a	(17)
5			2b	180	5	(63)	+	6b	(28)
7	3.0[20]	4.1[18]	2a	125	7	(78)	+	8a	(17)
7			2b	125	7	(67)	+	8b	(26)
7			2c	125	7	(70)	+	8c	(25)
9	2.98[21]	4.5[18]	2a	125	9	(95)	+	10a	(<5)
11	ca.2.5[22]	2.0[23]	2a	80(1h)	11	(70)	+	12	(21)

The experimental results allow the following reactivity series for the reactions of heterocyclic trimethylsilyl carboxylates with aldehydes to be deduced:



Comparisons of the reactivities of the compounds 5, 7, and 9, which have comparable basicities (Table III), clearly illustrate the influence of anion stabilization: reactivity increases with the stability of the corresponding hetaryl anion. In contrast, the higher reactivity of 1a towards 5 is unambiguously a result of the higher basicity of 1a towards 5.

In summary, it can be stated that the carbodecarboxylation of heterocyclic trimethylsilyl carboxylates with aldehydes or ketones is an interesting and preparatively useful alternative to the Hammick reaction of the corresponding carboxylic acids and to reactions of organometallic compounds.

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Experimental

Melting points were determined in small sealed tubes on a Büchi SMP 20 apparatus with a silicon oil bath and are uncorrected. ^{1}H NMR spectra were recorded on Varian T 60, A 60, or EM 360 and Bruker WP 80, HX 90, or CXP 300 spectrometers. Chemical shifts are reported in parts per million relative to Me_4Si as an internal standard in $CDCl_3$.

General Method for the Silylation of Hetaryl-carboxylic Acids with 1,1,1,3,3,3-Hexamethyldisilazane (HMDS)

HMDS (32.3 g, 0.20 mol) was slowly added dropwise to the stirred carboxylic acid (24.8 g, 0.20 mol) at room temperature under an anhydrous atmosphere. The mixture then was slowly warmed until a violent gas evolution occurred. After further stirring at higher temperature, absolute diethyl ether or n-pentane was added to the cooled mixture. The precipitate was separated by filtration, the filtrate was evaporated, and the residue purified by distillation. Elemental and ^{1}H NMR analyses of the colorless oils obtained were consistent with the expected data.

After work-up were obtained:
from 2-pyridinecarboxylic acid: 1a (35.7 g, 91%), b.p. 48°C/0.01 torr (lit. (24) b.p. 91°C/2 torr).
from 3-pyridinecarboxylic acid: 1b (37.7 g, 97%), b.p. 46°C/0.01 torr.
from 4-pyridinecarboxylic acid: 1c (38.4 g, 98%), b.p. 41°C/0.005 torr, (lit. (25) b.p. 62°C/0.02 torr), m.p. 36°C.
from 2-pyrazinecarboxylic acid: 5 (36.0 g, 92%), b.p. 112°C/11 torr.
from 3-pyridazinecarboxylic acid: (18.6 g, 0.15 mol) and HMDS (24.2 g, 0.15 mol): 7 (26.8 g, 91%), b.p. 93°C/0.001 torr, m.p. 64-65°C.
from 4-pyrimidinecarboxylic acid: (6.2 g, 50.0 mmol) and HMDS (21.1 g, 75.0 mmol): 9 (7.7 g, 79%), b.p. 105°C/9 torr, m.p. 63-64°C.

General Method for the Ipso Substitution of the Heterocyclic Trimethylsilyl Carboxylates 1, 5, 7, and 9 with Aldehydes 2a-d or Diphenyl Ketone (2e) to (Trimethylsiloxyalkyl)-substituted Hetarenes 3, 6, 8, and 10

The starting materials were stirred and heated in a round-bottom flask equipped with a septum-seal on one neck, a magnetic stirrer, reflux condenser with a bubble counter (purged with nitrogen), and a drying tube (sicapent, Merck). For reaction conditions, see Tables I and II. The progress of the reaction was monitored by ^{1}H NMR. For work-up, the reaction mixture was drawn out of the flask with a syringe through the septum, poured into a flame-dried distillation apparatus under nitrogen, and fractionated in vacuo. Elemental and ^{1}H NMR analyses of the compounds obtained were consistent with the expected data

After work-up were obtained:
from 1a (7.81 g, 40.0 mmol) and benzaldehyde (2a) (8.49 g, 80.0 mmol): 3a (9.56 g), b.p. 78°C/0.001 torr (lit. (26) b.p. 86°C/0.03 torr).
from 1a (7.81 g) and 4-methoxybenzaldehyde (2b) (10.89 g, 80.0 mmol): 3b (8.42 g), b.p. 116°C/0.01 torr.
from 1a (7.81 g) and n-decanal (2e) (10.50 g, 80.0 mmol): 3c (9.04 g), b.p. 82°C/0.001 torr.
from 1a (7.81 g) and diphenyl ketone (2e) (14.58 g, 80.0 mmol): 3e (8.1 g), b.p. 130°C/0.001 torr.
from 5 (7.85 g, 40.0 mmol) and 2a (8.49 g): 6a (5.19 g), b.p. 78°C/0.001 torr.
from 5 (7.85 g) and 2b (10.89 g): 6b (6.03 g), b.p. 123°C/0.005 torr, m.p. 35-55°C.
from 5 (7.85 g) and 2e (14.58 g): 6e (3.07 g), b.p. 130°C/0.001 torr.
from 7 (3.93 g, 20.0 mmol) and 2a (42.4 g, 30.0 mmol): 8a (3.48 g), b.p. 85°C/0.001 torr, m.p. 45-47°C.
from 7 (3.93 g) and 2b (5.45 g, 40.0 mmol): 8b (4.69 g), b.p. 124°C/0.001 torr.
from 7 (3.93 g) and 4-chlorobenzaldehyde (2d) (5.62 g, 40.0 mmol): 8d (4.11 g), b.p. 110°C/0.001 torr, m.p. 63-64°C.
from 9 (1.96 g, 10.0 mmol) and 2a (2.12 g, 20.0 mmol): 10a (1.70 g), b.p. 140-142°C/8 torr, m.p. 30-31°C.

General Method for the Hydrolyses of the (Trimethylsiloxyalkyl)hetarenes 3b,e (0.5 mmol) with Ethanol (100 ml) and Pyridinium Trifluoroacetate as Catalyst:

The components were heated under reflux for 24 h, the resulting solution was then concentrated in a rotation evaporator, the residue was treated with n-pentane, and the product obtained by cooling.
After work-up were obtained:
from 3b (1.44 g): 4-Methoxyphenyl-(pyridin-2-yl)-methanol (4b) as colorless crystals (1.04 g, 97%), m.p. 132-133°C (lit. (25) 131.5°C).
from 3e (1.67 g): Diphenly-(pyridin-2-yl)-methanol (4e) (1.26 g, 96%), m.p. 108-107°C (lit. (27) 105°C).

Trimethylsilyl 2-Pyridinecarboxylate 1-Oxide (11): The solution of sodium hydroxide (4.0 g, 0.10 mol) in water (titrisol, Merck) was slowly added to 2-pyridinecarboxylic acid 1-oxide at 0°C, then the mixture was stirred for 3 h at room temperature, and the resulting yellowish solution evaporated in a rotation evaporator. The yellowish residue was powdered and dried for 15 h in vacuo over phosphorus pentoxide at 95-105°C to yield 16.01 g (99%) of the sodium salt of 2-pyridinecarboxylic acid 1-oxide.

A solution of chlorotrimethylsilane (3.16 g, 30.0 mmol) in absolute diethyl ether (15 ml) was added dropwise to a stirred suspension of the sodium salt of 2-pyridinecarboxylic acid 1-oxide (3.22 g, 20.0 mmol) in absolute diethyl ether (40 ml) at 0°C within 2 h. After being stirred at room temperature for 24 h, the mixture was sonicated several times, the colorless precipitate was separated by filtration, and washed with absolute tetrahydrofuran (30 ml). The yellowish filtrate was evaporated to dryness on a rotation evaporator and the residue was dried in vacuo to yield 3.78 g (90%) of 11, m.p. 65-69°C (determined in a small sealed tube). ^{1}H NMR (DMSO-d_6, TMS ext.) 0.38 (s,9H,Si(CH_3)$_3$), 7.43-8.03 (m,3H,3-,4-,5-H), 8.38-8.58 (m,1H,6-H).
Anal. Calcd. for $C_9H_{13}NO_3Si$: C, 51.16; H, 6.20; N, 6.63. Found: C, 51.3; H, 6.09; N, 6.76.

2-(Phenyltrimethylsiloxymethyl)-pyridine 1-Oxide (12): From 11 (4.23 g, 20.0 mmol) and benzaldehyde (2a) (4.24 g, 40.0 mmol) analogous to the general method for the ipso substitution of heterocyclic trimethylsilyl-carboxylates. Yield after 17 h at 80°C and 4 h at 120°C: 12 as yellowish oil (3.39 g, 62%), b.p. 118°C/0.001 torr, m.p. 69-70°C (determinated in a small sealed tube). ^{1}H NMR ($CDCl_3$, TMS ext.) 0.05 (s,9H,Si(CH_3)$_3$), 6.48 (s,1H,PhC<u>H</u>), 6.98-7.86 (m,8H,Ph,3-,4-,5-H), 8.06-8.23 (m,1H,6-H).
Anal. Calcd. for $C_{15}H_{19}NO_2Si$: C, 65.90; H, 7.00; N, 5.13. Found: C, 66.65; H,6.80; N, 5.20.

2-(Phenylhydroxymethyl)-pyridine 1-Oxide (13): 12 (1.37 g, 5.0 mmol), ethanol (50 ml), and a trace of HCl were heated under reflux for 3 h, the resulting solution was concentrated in a rotation evaporator, and the residue purified by recrystallization from ethanol/n-pentane (1:1) to yield 13 as yellowish crystals (0.96 g, 95%), m.p. 165-166°C (lit. (26) m.p. 166-167°C).

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