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Journal of Organometallic Chemistry 553 (1998) 129–133

Journal of Organometallic Chemistry

Universal method for trimethylsilylation of acetylenic alcohols and glycols

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Received 14 May 1997

Abstract

A highly convenient universal method for trimethylsilylation of acetylenic alcohols and glycols via treatment by hexamethyldisilazane in the presence of benzoic acid sulphimide as a catalyst has been developed. The rate of trimethylsilylation of acetylenic alcohols is reduced from primary to secondary and to tertiary alcohols accordingly, as well as with the decreasing of hydroxyl nucleophylicity. The toxicity of trimethylsilyl acetylenic ethers, except 2-trimethylsiloxy-3-butyne, is much lower than that of original compounds. © 1998 Elsevier Science S.A.

Keywords: Trimethylsilylation; Acetylenic alcohols; Acetylenic glycols

1. Introduction

Silylation of organic compounds is widely applied for the protection of hydroxyl group in organic synthesis [1–3]. Trimethylsilyl ethers of some biologically active compounds are used in pharmacology [4]. Thus, anabolic drugs such as 17α-(trimethyl siloxy)androst-4-en-3-one, patented as Silandron [5] and 17-O-trimethylsilyl ether of 19-nortestosterone patented as Silabolin [6] are more effective than original 17-hydroxy compounds. This effect may be explained by a better penetration of silicon ethers through lipid cell membranes. Silyl ethers are easily hydrolyzed within the cells to form the initial compounds. Trimethylsilylation of acetylenic alcohols and glycols is far from being solved. So far, a universal method for the preparation of trimethylsilyl ethers of various acetylenic alcohols has not been developed. Silylation of propargyl alcohol with trimethylchlorosilane in the presence of base has been studied in more detail [7–10]. To this point, the silylation of tertiary acetylenic alcohols in ordinary ways was not successful, and secondary acetylenic alcohols are difficultly silylated. Thus, the interaction of 3-methyl-1-butyn-3-ol with methylphenylsilane, even in the presence of the Speier's catalyst in refluxing benzene, gives the corresponding trimethylsilyl ether in minor yield (11%) [11]. Silyl ethers of primary, secondary and tertiary α- and β-acetylenic alcohols were prepared by the reaction of their trialkylstannyl ethers with Me3SiCl [12].

1,1,1,3,3,3-Hexamethyldisilazane (HMDS) is widely used as a silyl donor due to the possibility to carry out the reaction in mild conditions with liberation of gaseous ammonia. Trimethylsilylation of alcohols with HMDS alone usually proceeds slowly and therefore the process is activated by addition of acids, bases or salts of ammonia [13,14]. The possibility to use the benzoic acid sulphimide (saccharin) as a catalyst for the trimethylsilylation of saturated alcohols is described [14].

2. Results and discussion

Our aim is to work out a universal method for the trimethylsilylation of acetylenic alcohols and glycols. We have studied the reaction of primary, secondary and tertiary acetylenic alcohols **1a**–**e** and glycols **3**, **5** with HMDS and benzoic acid sulphimide as a catalyst.

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The reasons for the preparative trimethylsilylation of acetylenic alcohol involve: (a) stoichiometric ratio of reactants; (b) with no solvent, if the alcohols **1a**–**f**, react because these reagents act as their own polar solvents. Crystalline 2-butyne-1,4-diol (**3**) and 5-methyl-3-nonyne-1,5-diol (**5**) were dissolved in suitable solvents: dimethylsulphoxide (DMSO) (**3**) and trichloromethane (**5**); (c) 1 mol% of saccharin; (d) temperature of the reaction mixture is 70°C, mainly for the removal of ammonia and driving the reaction to the right. The silylation of **5** at both functional groups was carried out in refluxing chloroform.

$$\underset{\mathbf{1}}{RC{\equiv}CCR^1R^2OH} \xrightarrow[\text{saccharin}]{\text{HMDS}} \underset{\mathbf{2}}{RC{\equiv}CCR^1R^2OSiMe_3} \qquad (1)$$

$R = R^1 = R^2 = H$(**a**); $R = R^1 = H$, $R^2 = Me$(**b**); $R^1 = R^2 = Me$(**c**); $R = Me_3Si$, $R^1 = R^2 = H$(**d**); $R = Et_3Ge$, $R^1 = R^2 = H$(**e**)

1-Pentyn-4-ol (**1f**) reacts analogously to the Scheme 1.

$$\underset{\text{1f}}{HC{\equiv}CCH_2CH(OH)Me} \xrightarrow[\text{saccharin}]{\text{HMDS}} \underset{\text{2f}}{HC{\equiv}CCH_2CH(OSiMe_3)Me} \qquad (2)$$

The reactivity of compounds was controlled by GLC. The yields of trimethylsilyl ethers **2a**–**f** are 93–99%. The structure of synthesized ethers **2a**–**f** was proved by ^1H, ^{13}C, ^{29}Si NMR spectroscopic data (Table 1) and IR Spectra (film): ν(C≡C) 2086–2100, 2165 cm^{-1} (**2d**, **e**); ν(Si–O–C) 1037–1086 cm^{-1} (Table 2).

The yield of trimethylsilyl ethers **2a**–**f** considerably depends on the structure of initial acetylenic alcohol (Table 3). Thus, 2-methyl-3-butyn-2-ol (**1c**) shows no reaction with HMDS alone at room temperature, whereas 2-propyn-1-ol (**1a**) gives trimethylsilyl ether **2a** in 94% yield for 10 h at the same temperature. The use of

Table 1
^1H, ^{13}C, ^{29}Si NMR data of the synthesized trimethylsilyl ethers **2a**–**f**, **4**, **6**, **7**

Compound	^1H NMR[a] δ (ppm)	^{13}C NMR[a] δ (ppm)	^{29}Si NMR[a] δ (ppm)
2a	4.28 (d, J = 2.5 Hz, 2H, $-CH_2$) 2.39 (t, J = 2.5 Hz, 1H, HC≡) 0.17 (s, 9H, $Si(CH_3)_3$)	82.26(HC≡*C*) 73.16(H*C*≡C) 50.85(CH_2) −0.33 ($Si(CH_3)_3$)	21.6
2b	4.51 (qd, J = 6.6 Hz and 2.2 Hz, 1H, CH) 2.38 (d, J = 2.2 Hz, 1H, HC≡) 1.44 (d, J = 6.6 Hz, 3H, CH_3) 0.17 (s, 9H, $Si(CH_3)_3$)	86.23(HC≡*C*) 71.66(H*C*≡C) 58.40(CH) 25.36(CH_3) 0.13($Si(CH_3)_3$)	19.1
2c	2.40 (s, 1H, HC≡) 1.49 (s, 6H, CH_3) 0.19 (s, 9H, $Si(CH_3)_3$)		13.5
2d	4.20 (s, 2H, CH_2) 0.17 (s, 18H, $Si(CH_3)_3$))	103.57(SiC≡*C*) 89.78(Si*C*≡C) −0.15 ($(CH_3)_3SiC$≡) −0.35 ($OSi(CH_3)_3$)	21.4(Si–O) −18.1(Si–C≡)
2e	4.31 (s, 2H, CH_2) 0.81–1.16 (m, 15H, C_2H_5) 0.18 (s, 9H, $Si(CH_3)_3$)		21.1
2f	3.96 (s, J = 6.2 Hz, 1H, CH) 2.28 (dd, J = 6.2 and 2.6 Hz, 2H, CH_2) 1.99 (t, J = 2.6 Hz, 1H, HC≡) 1.25 (d, J = 6.2 Hz, 3H, CH_3) 0.13 (s, 9H, $Si(CH_3)_3$)	81.68(HC≡*C*) 69.91 (H*C*≡C) 67.37(CH) 29.39 (CH_2) 23.22(CH_3) 0.13($Si(CH_3)_3$)	19.1
4[b]	4.31 (s, 4H, CH_2) 0.16 (s, 18H, $Si(CH_3)_3$)		21.0
6	4.32 (brs, 1H, OH) 3.68 (t, J = 7 Hz, 2H, CH_2O) 2.42 (t, J = 7 Hz, 2H, CH_2) 0.93–1.44 (m, 12H, CH_3, n C_4H_9)		18.3
7	3.68 (t, J = 6.8 Hz, 2H, CH_2O) 3.27 (brs, 1H, OH) 2.42 (t, J = 6.8 Hz, 2H, CH_2) 0.93–1.44 (m, 12H, CH_3, n C_4H_9) 0.14 (s, 18H, $Si(CH_3)_3$)		18.7

[a] In $CDCl_3$.
[b] In DMSO-d_6.

Table 2
Data for the trimethylsiyl ethers **2a**–**f** and **7**

Compound	B.p. (°C/mm Hg)	n_D^{20}	IR (cm^{-1})		Elemental analyses found (calc.) (%)		
			ν (C≡C)	ν (Si–O–C)	C	H	Si (Ge)
2a	59 (50)	1.4080	2086	1057	56.08 (56.18)	9.04 (9.04)	21.76 (21.85)
2b	109	1.4044	2093	1086	59.46 (59.46)	10.64 (9.94)	19.19 (19.74)
2c	116	1.4075	2100	1036	61.09 (61.48)	10.66 (10.32)	18.54 (17.97)
2d	65.5 (11)	1.4291	2164	1079	54.18 (53.92)	10.33 (10.07)	27.60 (28.02)
2e	74 (8)	1.4573	2165	1086	50.64 (50.07)	9.87 (9.76)	9.15 (9.76)
2f	59 (33)	1.4118	2106	1064	62.52 (62.74)	10.31 (10.30)	17.62 (17.96)
7	81 (1)	1.4588	2229	1057	61.66 (61.13)	10.07 (10.81)	17.62 (17.90)

saccharin in 1 mol% permits the reaction to be significantly promoted. The trimethylsilylation of propargyl alcohol (**1a**) at 70°C was completed for 0.5 h in 99% yield of **2a**. Tertiary alcohol **1c** gives 93% of **2c** for 2.5 h under the same conditions. The reaction time was reduced to 2 h at 70°C in the latter case (93% yield of **2c**). The silylation of 3-butyn-2-ol (**1b**) proceeds for 2 h at 70°C (yield 91%).

So we observed the high sensitivity of trimethylsilylation to the steric environment of acetylenic alcohols. The ease of silylation of α-acetylenic alcohols decreases in order: primary > secondary > tertiary. The remoteness of the triple bond from the reactive centre improves the reactivity of the latter towards HMDS, that should be ascribed to the increase of hydroxyl nucleophilicity. As seen from Table 3, the β-acetylenic alcohol 4-pentyn-2-ol (**1f**) is silylated twice as fast as α-analog of **1b** (1 h, 98% and 2 h, 91%, respectively). This difference in reactivity of acetylenic alcohols (according to the structure) is determined by steric and electronic influence of substituent at the carbon atom containing hydroxyl group.

3-Trimethylsilyl- and 3-triethylgermyl-2-propyn-1-ols, (**1d**,**e**) show a considerably different reactivity towards HMDS in the presence of saccharin. The ease of silylation of **1e** (R = Et_3Ge) and propargyl alcohol (**1a**) is practically identical. At the same time, the silicon analog **1d** reacts with HMDS four times more slowly. This difference is determined by higher nucleophilicity of 3-triethylgermyl-2-propyn-1-ol (**1e**) in comparison with the silicon analog **1d** [15]. 3-Trimethylsiloxy-2-propyne (**2a**) was used in the synthesis of organometallic acetylenic alcohols **1 d**–**f** in high yields 85–87% [16] whereas these compounds were prepared from bis(bromomagnesium) derivatives of **1a** in 40–54% yield [17,18]:

$$\underset{\mathbf{2a}}{HC{\equiv}CCH_2OSiMe_3} \xrightarrow[2.\,R_3SiCl\ or\ R_3GeBr\ \ 3.\,H_3O]{1.\,EtMgBr} \underset{\mathbf{1}}{R_3MSiC{\equiv}CCH_2OH} \qquad (3)$$

M = Si, R = Me **1d**; M = Ge, R = Et **1e**; M = Si, R = Et **1g**.

The advantage of the method [16] is a good solubility of 3-bromomagnesium-1-trimethylsiloxy 2-propyne in Et_2O unlike to with low-soluble 1,3-bis(bromo magnesium) derivative of **1a**.

The influence of catalyst concentration on the efficiency of alcohols silylation was illustrated with 2-methyl-3-butyn-2-ol (**1c**). The increase in the amount of saccharin from 1 to 5 mol% at 70°C allows to accelerate the reaction approximately 3.5 times (yield of **2c** 90–98%). However, less hindered alcohols as primary **1a**, **d**, **e** and secondary **1b**, **f** are readily silylated by the addition of 1 mol% of saccharin for 0.5–2 h in 91–95% yield of TMS ethers **2a–f**.

It is known that *N*,*O*-bis(trimethylsilyl)sulphamate $Me_3SiNHSO_3SiMe_3$ is a very efficient silyl donor [19]. Nevertheless, our attempt to use it for the trimethylsilylation of **1b** has not been successful because of oligomerization of the reaction mixture. Probably, alcohol **1b** will undergo an acid-catalyzed acetylene-allenic rearrangement to an unstable, easily polymerized product [20]. The trimethylsilylation of 2-butyn-1,4-diol (**3**) in an appropriate solvent (DMSO) in the presence of 1 mol% of saccharin is completed for 5 h. The yield of 1,4-bis(trimethylsiloxy)-2-butyne (**4**) is 90%.

$$\underset{\mathbf{3}}{HOCH_2C{\equiv}CCH_2OH} \xrightarrow[\text{saccharin}]{\text{HMDS}} \underset{\mathbf{4}}{Me_3SiOCH_2C{\equiv}CCH_2OSiMe_3} \qquad (4)$$

Table 3
Reaction conditions and yields of trimethylsilyl ethers **2a**–**f**, **4**, **6**, **7**

Compound	Amount of catalyst (mol %)	Reaction time (h)	Temperature (°C)	Yield (%)
2a	–	10.0	25	94
	1	0.5	70	99
2b	1	2.0	70	91
2c	–	10.0	25	–
	1	2.5	70	93
	2	2.0	70	98
	3	1.5	70	97
	5	0.75	70	90
2d	1	2.0	70	98
2e	1	0.5	70	99
2f	1	1.0	70	98
4	1	5.0	70	90
6	–	6.0	25	90
7	1	6.0	70	92

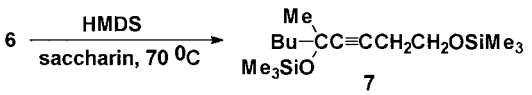
Table 4
The toxicity of acetylenic alcohols and their trimethylsilyl ethers

No.	Compound	DL_{50} mg/kg	No.	Compound	DL_{50} mg/kg
1a	$HC{\equiv}CCH_2OH$	100	**2a**	$HC{\equiv}CCH_2OSiMe_3$	650
1b	$HC{\equiv}CCH(OH)Me$	200	**2b**	$HC{\equiv}CCH(OSiMe_3)Me$	1000
1c	$HC{\equiv}CC(OH)Me_2$	200	**2c**	$HC{\equiv}CC(OSiMe_3)Me_2$	175
1f	$HC{\equiv}CCH_2CH(OH)Me$	350	**2f**	$HC{\equiv}CCH_2CH(OSiMe_3)Me$	400
1d	$Me_3SiC{\equiv}CCH_2OH$	150	**2e**	$Et_3GeC{\equiv}CCH_2OSiMe_3$	500

A necessary condition for the preparation of **4** in high yield is to remove ammonia from the reaction mixture by distillation with benzene. Otherwise the yield of **4** does not exeed 70% even if the reaction time is increased. The reactivity of **4** towards HMDS is much lower than that of 2-propyn-1-ol (**1a**) due to higher nucleophilicity of the latter.

The high sensitivity of silylation to steric factors was used for the selective protection of primary hydroxyl group in 5-methyl-3-nonyn-1,5-diol (**5**) [21]. Thus, the silylation of **5** by HMDS alone in dichloromethane at 10–25°C was realized with regioselective formation of 1-trimethylsiloxy-5-methyl-3-nonyn-5-ol (**6**) in 87% yield fixed by GLC. With a raising of temperature from 10°C to ambient reaction (**5**) is accelerated more than twice. The trimethylsilylation of both hydroxyl groups in **5** leads to 1,5-bis(trimethylsiloxy)-5-methyl-3-nonyne (**7**) (reaction 6). The latter was obtained in 92% yield in the presence of 1 mol% of saccharin under reflux in $CHCl_3$ for 6 h. The structure of monotrimethylsilyl ether (**6**) was proved by its transformation in **7**, and by IR spectra (Table 2).

5 6 (5)



7 (6)

As seen from Table 4, trimethylsilyl ethers **2a**, **b**, **f** are less toxic than the starting alcohols **1a**, **b**, **f**. The toxicity of 1-trimethylsiloxy-2-propyne (**2a**) and 2-trimethylsiloxy-3-butyne (**2b**) are five and six times lower than those for alcohols **1a**, **b**. In the cases of 2-trimethylsiloxy-2-methyl-3-butyne (**2c**), 2-trimethylsiloxy-4-pentyne (**2f**) and corresponding alcohols **1c**, **1f** the toxicity is similar.

3. Experimental details

^1H, ^{13}C, ^{29}Si NMR spectra were recorded using JEOL-FX-90Q spectrometer (^{13}C, 22.49 MHz; ^{29}Si, 17.75 MHz). Chemical shifts were measured relative to the internal standard tetramethylsilane. Samples were analized in $CDCl_3$ or DMSO-d_6 solution. IR spectra were recorded on an IR-75 Spectrometer (liquid film). GLC analysis was carried out on a Chromatograph LKhM-80 with 3 m columns packed with PMS on Chromaton. The alcohols 3-butyn-2-ol (**1b**), 2-methyl-3-butyn-2-ol (**1c**), 4-pentyn-2-ol (**1f**) were prepared by reaction of sodium acetylide with the corresponding carbonyl compounds or propylene oxide in liquid ammonia by a method described in [21,22]. *N,O*-bis(trimethylsilyl)sulphamate was prepared by a method described in [19]. The solvents ($CHCl_3$, DMSO) were dried and distilled, HMDS was carefully fractionated to 98.5% purity.

*3.1. General procedure for the trimethylsilylation of acetylenic alcohols **1a–f***

Saccharin (0.36 g, 1 mol%) was added to a stirred solution of alcohol **1a–f** (200 mmol) and 16.3 g (100 mmol) of HMDS at room temperature. The temperature of the reaction mixture exothermally arose to 40°C. Then the mixture was heated to 70°C to the completion of the reaction (cessation of ammonia evolution, GLC control). Trimethylsilyl ethers **2a–f** were isolated by distillation in vacuo.

3.2. 1,4-bis(trimethylsiloxy)-2-butyne (4)

To a stirred solution of 2-butyne-1,4-diol (**3**) (8.6 g, 100 mmol) in 20 ml of DMSO, saccharin (0.36 g, 1 mol%) and HMDS (16.3 g, 100 mmol) were added and the reaction mixture was heated at 70°C for 5 h. Benzene (6 ml) was added to remove ammonia from the mixture and azeotrope ammonia–benzene was distilled every 2 h. The yield of **4** (90%) was determined by GLC. Pure compound **4** was not isolated because of close boiling points of **4** and DMSO.

3.3. 1-Trimethylsiloxy-5-methyl-3-nonyn-5-ol (6)

To the solution of **5** (1.7 g, 10.0 mmol) in 5 ml of $CHCl_3$ was added HMDS (0.8 g, 5.0 mmol). The reaction mixture was stirred at room temperature for 6.5 h, then concentrated to give **6** (control by GLC), IR (film): ν(SiO–C) 1080, ν(C≡C) 2240, ν(OH) 3370

cm^{-1}. The attempt to distil **6** in vacuo leads to a mixture of **6** and **7**.

3.3.1. 5-Methyl-1,5-bis(trimethylsiloxy)-3-nonyne (7)

To the solution of crude **6** (2.4 g, 10.0 mmol) in 5 ml $CHCl_3$, saccharin (0.018 g, 1 mol%) and HMDS (0.8 g, 5.0 mmol) were added. The mixture was heated at reflux for 6 h. The solvent was evaporated and the residue was distilled in vacuo to give **7** (2.88 g, 92%).

3.4. 3-Triethylgermyl-2-propyn-1-ol (1e)

To a Grignard reagent (Mg 24.0 g, 1.0 mol; EtBr 109.0 g, 1.0 mol; 300 ml of Et_20) of **2a** (128.3 g, 1.0 mol) in 100 ml Et_2O was added on an ice bath cooling. The reaction mixture was stirred at room temperature for 3 h and Et_3GeBr (237.0 g, 1.0 mol) in 150 ml of Et_2O was added. The mixture was stirred for 3 h, neutralized with aqueous $NaHCO_3$ solution, extracted with Et_2O and dried over Na_2SO_4. The solvent was evaporated and the residue was distilled in vacuo to give **1e** (194.0 g, 85%). B.p. 90–92°C/3 mm Hg, n_D^{20} 1.4841. IR (film): ν(C≡C) 2185, ν(OH) 3380 cm^{-1}. [21]: B.p. 112°C/9 mm Hg, n_D^{20} 1.4822. 3-Trimethylsilyl-2-propyn-1-ol (**1d**) and 3-triethylsilyl-2-propyn-1-ol (**1g**) were prepared similarly in 86 and 87% yield, respectively.

Acknowledgements

This work was supported by the Russian Foundation of Basic Research, grant 95-03-09302a.

References

[1] R. Tacke, H. Linon, Bioorganosilicon chemistry, S. Patai, Z. Rappoport (Eds.), Chap. 18, Wiley, New York, 1989.
[2] A.E. Pierce, Silylation of Organic Compounds, Pierce Chemical, Rockford, IL, 1968.
[3] M.M. Demina, A.A. Velikanov, A.S. Medvedeva, O.I. Margorskaya, M.G. Voronkov, Pat. SSSR 1833392 (1991). Bull. Izobret. No. 29 (1993) 146.
[4] M.G. Voronkov, J.I. Zelchan, E. Lukevitz, Silizium und Leben, Academie-Verlag, Berlin, 1975.
[5] S. Pavlenko, Organosilicon Chemistry, Berlin, New York, 1986, p. 133.
[6] A.A. Shishkina, G.I. Ivanenko, N.A. Zarubina, O.N. Volzhina, V.G. Angarskaya, K.K. Pivnitsky, Khimiko-Farm. Zh. 20 (1986) 232.
[7] E.O. Tsetlyna, S.F. Pavlov, I.M. Korotaeva, Jzv. Akad. Nauk SSSR, Ser. Khim. (1974) 2856.
[8] V.F. Mironov, N.G. Maximova, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk (1960) 2059.
[9] P. Brison, M. Liford, Ger. Offen, 1,1954,961, C.A. 73 (1970) 14978u.
[10] K.A. Andrianov, I.A. Shikhiev, J.F. Nasirov, E.M. Movsumzade, M.I. Shikhieva, R.Yu. Gasanova, Dokl. Akad. Nauk SSSR 215 (1974) 1117.
[11] L.G. Kulieva, R.M. Mustafaeva, S.I. Sadykhzade, Zh. Vses. Khim. Obshchestva 29 (1984) 231.
[12] M.F. Shostakovsky, R.G. Mirskov, V.M. Vlasov, Sh.I. Tarpishchev, Zh. Obshch. Khim. 37 (1967) 1738.
[13] M.D. Mizhiritsky, Yu.A. Yuzhelevsky, Usp. Khim. 56 (1987) 609.
[14] C.A. Bruynes, T.K. Jurriens, J. Org. Chem. 47 (1982) 3966.
[15] A.N. Egorochkin, O.I. Margorskaya, S.E. Skobeleva, A.S. Medvedeva, A.I. Borisova, N.S. Vyazankin, Izv. Akad. Nauk SSSR, Ser. Khim. (1986) 1789.
[16] A.S. Medvedeva, O.I. Margorskaya, M.G. Voronkov, Inventor's Certificate SSSR, 1705297 (1989). Bull. Izobret. No. 2 (1992) 102.
[17] I.A. Shikhiev, I.A. Aslanov, B.G. Yusupov, Zh. Obshch. Khim. 31 (1961) 3647.
[18] M.F. Shostakovsky, N.V. Komarov, O.G. Yarosh, Izv. Akad. Nauk SSSR, Ser. Khim., (1966) 101.
[19] B.E. Cooper, I. Westall, J. Organomet. Chem. 118 (1976) 135.
[20] M.V. Mavrov, V.F. Kucherov, Usp. Khim. 36 (1967) 553.
[21] M.F. Shostakovsky, V.M. Vlasov, A.S. Lozhenitsyna, A.A. Gavrilovskaya, Izv. Akad. Nauk SSSR, Ser. Khim. (1965) 709.
[22] M.F. Shostakovsky, V.M. Vlasov, A.S. Medvedeva, G.G. Chickareva, M.M. Loshina, Inventor's Certificate SSSR, 193493 (1967), C.A. 69 (1968) 18594f.