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GENERAL ACCESS TO A NOVEL CLASS OF SILYL HETEROCYCLES

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2-Trimethylsilyl-substituted five-membered heterocycles can be accessed through the reaction of bromo(methoxy)methyltrimethylsilane with 1,2-dithiols, 1,2-mercapto alcohols, 1,2-mercapto amines, and 1,2-hydroxy amines, leading to the formation of several 2-silylated 1,3-dithiolanes, -oxathiolanes, -thiazolidines, and -oxazolidines.

Keywords: dithiolanes, organosilanes, oxathiolanes, oxazolidines, silyl heterocycles, thiazolidines.

Five-membered ring heterocyclic derivatives are valuable intermediates in organic synthesis. Compounds containing either one heteroatom, as furans and pyrrolidines, or two or more heteroatoms have played an important role in different synthetic strategies. Among these the last structures 1,3-dioxolanes, [1, 2] 1,3-oxathiolanes, [3] 1,3-thiazolidines, 1,3-oxazolidines, imidazolines, and benzotriazole derivatives [4–8] have found wide application as building blocks for the construction of more complex molecules [9].

Furthermore, the umpolung reactivity is a valuable synthetic strategy in organic synthesis providing unconventional access to molecules through the formation of bonds *via* the inversion of normal reactivity [10]. In this context the development of synthetic equivalents of acyl anions has recently actracted a great deal of interest for the synthetic potential that such reaction may disclose. In this connection suitably protected carbonyl derivatives, in particular heterocyclic derivatives, represent a very interesting class of compounds able to act as equivalents of acyl anions. For example, lithiated chiral oxazolidinones, including compounds derived from camphor [11], have been reported to react with aldehydes, ketones, and imines leading to enantioselective formylation of the carbonyl compounds [12, 13]. Oxazolidines also found application as chiral formyl anion equivalents, either for direct metalation in the presence of (–)-sparteine [14] or through transmetalation of tributylstannyl derivative with BuLi and condensation with benzaldehyde [15, 16]. Also thiazolidines upon treatment with BuLi and aldehydes or ketones in the presence of (–)-sparteine afforded products with high *ee* but moderate diastereoselectivity [17, 18]. Isopropyl N-Boc-thiazolidines have been used as chiral organolithium compounds in the addition to aldehydes, leading to products with good stereoselectivity [19]. Thiazolidines are also metalated with BuLi via their respective formamidines, but 40-50% fragmentation of the heterocyclic ring has been observed [20]. Chiral dioxolanes [15] and dioxolanones [2] also found application as acyl anion equivalents.

1,3-Dithianes have been also widely used in umpolung reactivity. They can be easily metalated with BuLi and reacted with a wide range of electrophiles, thus evidencing their behavior as useful synthons and umpoled reagents [21-27]; though several methods for their unmasking have been reported [28, 29],

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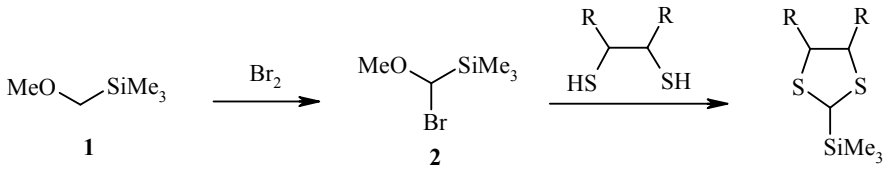
they still suffer from the generally harsh conditions of their unblocking. On the other hand, dioxolanes, oxathiolanes, dithiolanes, and thiazolidines have been reported to be unmasked under milder conditions, thus possibly giving a broader spectrum of application to such molecules in the generation of formyl and acyl anion equivalents. Unfortunately such heterocycles suffer generally from the difficulties in their functionalization under strong basic conditions. For instance, 1,3-dithiolanes, upon treatment with bases, have been reported to undergo either deprotonation at C-2 with subsequent cycloelimination to dithiocarboxylate anions and ethylene derivatives [30] or at C-4 to afford products derived from thiocarbonyl derivatives and vinyl thiolate anion [31, 32]. A similar behavior was evidenced in unsubstituted dioxolanes, whose anions undergo fragmentation. Thiazolidines are also reported to be metalated but only in the presence of specific nitrogen-protecting groups. Only two examples of functionalization under the basic conditions of dithiolanes bearing an electron withdrawing group are reported in the literature, thus evidencing the still present need for a general protocol for their functionalization [33-36]. Thus, taking advantage of the reactivity of organosilanes, which seems to occur *via* a pentacoordinated silicon species, and not a free carbanion, we envisaged that the functionalization of the C–Si bond in silyl heterocycles could possibly lead to the solution of this problem, and to the development of a novel and general functionalization methodology for such labile heterocycles [37].

As direct access to silyl heterocycles is difficult or even prevented, an alternative access to such molecules had to be devised.

A general access to silyl dithiolanes, and, more generally, to five-membered ring silylated heterocycles could be envisaged through the simple reaction of bifunctional molecules such as dithiols, amino alcohols, amino thiols, and mercapto alcohols with formyl trimethylsilane. The difficulties in the generation and handling of such a labile molecule [38] led to the search for a possible synthetic equivalent, and we envisaged the reagent of choice in bromo(methoxy)methyltrimethylsilane (**2**). Such molecule, in fact, can be obtained in quantitative yield by the treatment of the commercially available methoxymethyltrimethylsilane (**1**) with bromine [39-41] and subsequent *one-pot* treatment with the required thiol.

Thus, we reacted 1,2-ethanedithiol with bromomethoxy derivative **2**, and we were able to isolate in 72% yield the corresponding 2-trimethylsilyl-1,3-dithiolane (**3a**), which could be easily purified on TLC. This reaction evidenced the ability of compound **2** to act as a real synthetic equivalent of formylsilane and opened the way to a possible general route to access a wide variety of silyl heterocycles.



1 **2** **3a**,**b**

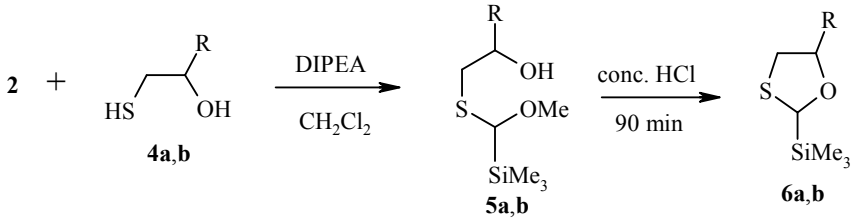
a R = H, **b** R = Me

In a similar way, by reacting *meso*-butane-2,3-dithiol both *cis* and *trans* diastereoisomers of *meso*-4,5-dimethyl-2-trimethylsilyl-1,3-dithiolane (**3b**) were isolated.

To study the generality of this reaction, the freshly prepared compound **2** was reacted *in situ* with β-mercaptoethanol (**4a**) at room temperature in the presence of diisopropylethylamine (DIPEA) and stirred overnight. In these conditions the intermediate compound **5a** was obtained. To achieve cyclization after stirring the reaction mixture overnight in the presence of DIPEA, conc. HCl was added in the same flask and the mixture was stirred for 90 min to obtain the desired 2-trimethylsilyl-1,3-oxathiolane (**6a**).

Due to the instability of these heterocycles under acidic conditions the treatment with HCl must not be longer than 90 min. If the intermediate product is treated under acidic conditions for a longer time, oxathiolane ring fragmentation was observed.

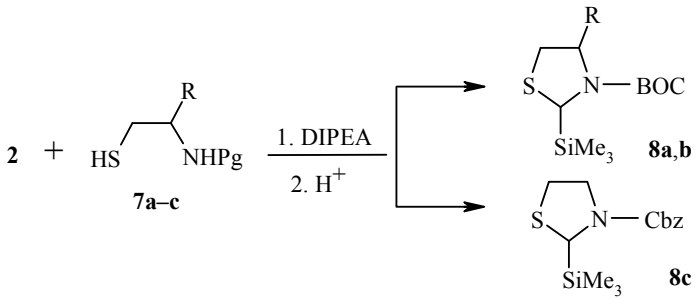
5-(Methoxymethyl)-2-trimethylsilyl--1,3-oxathiolane (**6b**) as a mixture of diastereoisomers (6:1) was obtained similarly.



a R = H, **b** R = CH_2OMe

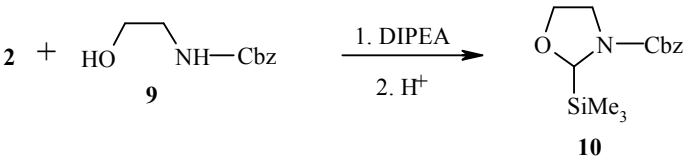
The reaction of silane **2** *in situ* with N-protected aminoethanethiols **7a**,**c** afforded smoothly 2-silyl-N-protected 1,3-thiazolidines **8a** and **8c**.

Moreover, in the reaction with N-Boc-protected 2-amino-4-methylpentane-1-thiol (**7b**) the substituted 4-isobutyl-N-Boc-2-trimethylsilylthiazolidine (**8b**) was obtained as an equimolar mixture of *cis* and *trans* isomers.



7 a R = H, Pg = BOC, **b** R = *i*-Bu, Pg = BOC, **c** R = H, Pg = Cbz; **8 a** R = H, **b** R = *i*-Bu

The treatment of compound **2** with a suitably N-protected 2-aminoethanol **9** led to the isolation of the N-Cbz-2-silyl-1,3-oxazolidine **10**.



In conclusion we have reported a novel and general protocol for the synthesis of a variety of silyl heterocycles through simple and high yielding procedures, thus opening the way to a thorough investigation of their chemistry.

EXPERIMENTAL

^1H and ^{13}C NMR spectra were recorded on a Varian Gemini 200 (200 and 50 MHz, respectively) and a Varian Mercury 400 (400 and 100 MHz, respectively) in $CDCl_3$ solutions. Chemical shifts are given relative to the residue signals of the solvent (^1H: 7.26 ppm; ^{13}C: 77.0 ppm). Mass spectra were obtained on a MFC500/QMD 1000 Carlo Erba instrument and a Shimadzu GCMS-QP5050/GC 17A apparatus with electron impact ionization (70 or 30 eV).

2-Trimethylsilyl-1,3-dithiolanes 3a,b (General procedure). A solution of bromine (2.57 mmol) in dry CCl_4 (4 ml) was added dropwise with stirring under N_2 to a solution of methoxymethyltrimethylsilane (2.57 mmol) in dry CCl_4 (5 ml). The mixture was stirred until the bromine disappeared. A solution of the suitable dithiol (2.57 mmol) in CH_2Cl_2 (5 ml) was then added and the mixture was stirred overnight. After

washing with water the organic layer was dried (Na_2SO_4) and evaporation of the solvent gave the crude product, which was purified by chromatography (column or TLC).

2-Trimethylsilyl-1,3-dithiolane (**3a**). TLC petroleum ether–diethyl ether, 20:1 (72%). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 0.18 (9H, s, $SiMe_3$); 3.06-3.29 (4H, m); 3.53 (1H, s, $HCSiMe_3$). ^{13}C NMR spectrum, δ, ppm: -2.3 ($Si(\underline{C}H_3)_3$); 37.6; 39.4. Mass spectrum, *m/z* (I_{rel}, %): 178 (41) $[M]^+$, 135 (97), 105 (72), 91 (25), 75 (63), 73 (100), 59 (81). Found, %: C 40.16; H 8.12. $C_6H_{14}S_2Si$. Calculated, %: C 40.40; H 7.91.

***meso*-4,5-Dimethyl-2-trimethylsilyl-1,3-dithiolane** (**3b**). TLC hexanes–ethyl acetate, 200:1 (82%). A mixture of the two isomers, 1:3. ***cis* Isomer**: ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 0.14 (9H, s, $SiMe_3$); 1.25-1.28 (6H, m); 3.50-3.64 (2H, m); 3.69 (1H, s, $HCSiMe_3$). ^{13}C NMR spectrum, δ, ppm: -2.5 ($Si(\underline{C}H_3)_3$); 16.5; 36.9; 53.2. Mass spectrum, *m/z* (I_{rel}, %): 206 (5) $[M]^+$, 150 (11), 135 (32), 73 (100), 59 (16). Found, %: C 46.20; H 8.90. $C_8H_{18}S_2Si$. Calculated, %: C 46.54; H 8.79. ***trans* Isomer**: ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 0.16 (9H, s, $SiMe_3$); 1.31 (6H, d, J = 6.6, CH_3); 3.62–3.75 (2H, m); 3.81 (1H, s, $HCSiMe_3$). ^{13}C NMR spectrum, δ, ppm: -2.6 ($Si(\underline{C}H_3)_3$); 15.5; 33.7; 53.4. Mass spectrum, *m/z* (I_{rel}, %): 206 (30) $[M]^+$, 163 (25), 150 (71), 135 (100), 73 (89), 59 (56). Found, %: C 46.32; H 9.06. $C_8H_{18}S_2Si$. Calculated, %: C 46.54; H 8.79.

2-Trimethylsilyl-1,3-oxathiolanes 6a,b (General procedure). A solution of freshly prepared bromo(methoxy)methyltrimethylsilane (**2**) (4.24 mmol) (obtained from methoxymethyl trimethylsilane and bromine in CCl_4) was slowly added at room temperature with a solution of the appropiate β-mercapto alcohol (4.24 mmol) and DIPEA (5.08 mmol) in 23 ml of anhydrous CH_2Cl_2. The mixture was stirred overnight and then treated with HCl 12M (5 ml) for 90 min. After dilution with CH_2Cl_2 and addition with water, the mixture was stirred for 5-10 min and then transferred into a separatory funnel. Solid $NaHCO_3$ was slowly added to neutralize the solution. The organic phase was washed with water (2 × 15 ml) and dried over Na_2SO_4. Evaporation of the solvent afforded crude compounds, which were chromatographically purified.

2-Trimethylsilyl-1,3-oxathiolane (**6a**). TLC petroleum ether–ethyl acetate, 4:1 (70%). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 0.13 (9H, s, $SiMe_3$); 2.79-2.93 (1H, m, HCHS); 3.03-3.12 (1H, m, HCHS); 3.49-3.62 (1H, m, HCHO); 4.37-4.47 (1H, m, HCHO); 4.50 (1H, s, $HCSiMe_3$). ^{13}C NMR spectrum, δ, ppm: -3.7 ($Si(\underline{C}H_3)_3$); 32.8 (CH_2S); 73.7 (CH_2O); 78.7 ($H\underline{C}SiMe_3$). Mass spectrum, *m/z* (I_{rel}, %): 163 (2) $[M+1]^+$, 162 (1) $[M]^+$, 134 (25), 119 (100), 89 (15), 73 (74). Found, %: C 44.22; H 8.74. $C_6H_{14}OSSi$. Calculated, %: C 44.39; H 8.69.

5-(Methoxymethyl)-2-trimethylsilyl-1,3-oxathiolane (**6b**). A mixture of diastereoisomers (6:1) was purified on TLC (petroleum ether–ethyl acetate, 100:1, 52%). **Major isomer:** ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 0.12 (9H, s, $SiMe_3$); 2.65 (1H, dd, J = 8.2, J = 10, HCHS); 3.09 (1H, dd, J = 6.0, J = 10, HCHS); 3.40 (3H, s, CH_3O); 3.44-3.61 (2H, m, CH_2O); 3.96-4.08 (1H, m, CHO); 4.65 (1H, s, $HCSiMe_3$). ^{13}C NMR spectrum, δ, ppm: -3.6 ($Si(\underline{C}H_3)_3$); 35.1 (CH_2S); 59.4 (CH_3O); 73.5 (CH_2O); 77.2 ($H\underline{C}SiMe_3$); 84.5 (CHO). Mass spectrum, *m/z* (I_{rel}, %): 206 (2) $[M]^+$, 146 (55), 135 (60), 119 (100), 91 (49), 73 (57), 59 (38). Found, %: C 46.38; H 8.84. $C_8H_{18}O_2SSi$. Calculated, %: C 46.56; H 8.79. **Minor isomer:** ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 0.12 (9H, s, $SiMe_3$); 2.82–2.88 (2H, m, CH_2S); 3.33–3.40 (2H, m, CH_2O, partially overlapped with signal at 3.38); 3.38 (3H, s, CH_3O); 4.38–4.51 (1H, m, CHO); 4.68 (1H, s, $HCSiMe_3$). ^{13}C NMR spectrum, δ, ppm: –3.5 ($Si(\underline{C}H_3)_3$); 39.9 (CH_2S); 59.3 (CH_3O); 72.7 (CH_2O); 77.2 ($H\underline{C}SiMe_3$); 82.1 (CHO). Mass spectrum, *m/z* (I_{rel}, %): 206 (1) $[M]^+$, 146 (21), 135 (32), 119 (100), 91 (23), 73 (63), 59 (24).

2-Trimethylsilyl-1,3-thiazolidines 8a–c (General procedure). To a freshly prepared solution of compound **2** (5 mmol) (obtained from methoxymethyltrimethylsilane and bromine in CCl_4) were added at room temperature anhydrous CH_2Cl_2 (10 ml), the appropriate N-protected 2-mercapto amine (5 mmol) dissolved in 5 ml of CH_2Cl_2, and DIPEA (1.2 eq). The mixture was stirred overnight, then treated with *p*-toluenesulfonic acid (0.1 eq) for 90 min. The resulting mixture was washed with water and brine, and the organic phase dried over Na_2SO_4. Evaporation of the solvent afforded the crude N-protected thiazolidines, which were purified by flash chromatography.

***tert*-Butyl 2-(trimethylsilyl)thiazolidine-3-carboxylate** (**8a**). Petroleum ether–ethyl acetate, 8:1 (81%). R_f 0.8. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 0.10 (9H, s, $SiMe_3$); 1.46 (9H, s, $(CH_3)_3$); 2.81-2.92 (2H, m, CH_2S);

3.10-3.30 (1H, m, HCHN); 4.10-4.35 (1H, m, HCHN); 4.60 (1H, s, $HCSiMe_3$). ^{13}C NMR spectrum, δ, ppm: -2.6 ($Si(\underline{C}H_3)_3$); 28.3; 30.5; 49.4; 50.9; 80.1; 154.0. Mass spectrum, *m/z* (I_{rel}, %): 263 (0.5) $[M+2]^+$, 204 (89), 188 (10), 160 (100), 132 (56), 100 (63), 88 (94), 73 (98). Found, %: C 50.30; H 9.05; N 5.08. $C_{11}H_{23}NO_2SSi$. Calculated, %: C 50.53; H 8.87; N 5.36.

***tert*-Butyl 4-isobutyl-2-(trimethylsilyl)thiazolidine-3-carboxylate** (**8b**). A mixture of diastereoisomers (1:1) was purified on TLC petroleum ether–ethyl acetate, 10:1 (53%). R_f 0.9 and 0.7. ***trans* Isomer:** ^1H NMR spectrum, δ, ppm (*J*, Hz): 0.12 (9H, s, $SiMe_3$); 0.95 (6H, d, *J* = 5.8, $CH(CH_3)_2$); 1.38-1.61 (3H, m, $CH_2CH(CH_3)_2$); 1.47 (9H, s, $(CH_3)_3$); 2.63 (1H, dd, *J* = 3.8, *J* = 11.6, HCHS); 3.02 (1H, dd, *J* = 6.4, *J* = 11.6, HCHS); 4.22-4.37 (1H, m, HCHN); 4.7 (1H, s, $HCSiMe_3$). ^{13}C NMR spectrum, δ, ppm: -1.9 ($Si(\underline{C}H_3)_3$); 21.9; 23.8; 25.8; 28.6; 36.1; 43.8; 52.3; 60.0; 80.0; 157.1. Mass spectrum, *m/z* (I_{rel}, %): 260 (07) $[M–57]^+$, 188 (5), 144 (7), 73 (56), 57 (100). Found, %: C 56.48; H 10.08; N 4.60. $C_{15}H_{31}NO_2SSi$. Calculated, %: C 56.73; H 9.84; N 4.41. ***cis* Isomer:** ^1H NMR spectrum, δ, ppm (*J*, Hz): 0.15 (9H, s, $SiMe_3$); 0.94 (6H, d, *J* = 5.8, $CH(CH_3)_2$); 1.40-1.59 (3H, m, $CH_2CH(CH_3)_2$); 1.46 (9H, s, $(CH_3)_3$); 2.65 (1H, dd, *J* = 2.0, *J* = 1.2, HCHS); 3.03 (1H, dd, *J* = 6.8, *J* = 11.2, HCHS); 4.10 (1H, s, $HCSiMe_3$); 4.26-4.36 (1H, m, HCHN). ^{13}C NMR spectrum, δ, ppm: -0.6 ($Si(\underline{C}H_3)_3$); 22.1; 23.5; 25.7; 28.5; 36.0; 42.4; 52.1; 59.5; 80.1; 157.1. Mass spectrum, *m/z* (I_{rel}, %): 260 $[M–57]^+$ (07), 188 (5), 144 (7), 73 (56), 57 (100). Found, %: C 56.60; H 9.98; N 4.39. $C_{15}H_{31}NO_2SSi$. Calculated, %: C 56.73; H 9.84; N 4.41.

Benzyl 2-(trimethylsilyl)thiazolidine-3-carboxylate (**8c**). Petroleum ether–ethyl acetate, 4:1 (56%). R_f 0.8. ^1H NMR spectrum, δ, ppm (*J*, Hz): 0.09 (9H, s, $SiMe_3$); 2.85-2.92 (2H, m, CH_2S); 3.23-3.42 (1H, m, HCHN); 4.11-4.37 (1H, m, HCHN); 4.61 (1H, s, $HCSiMe_3$), 5.09 (1H, d, *J* = 14, HCHPh); 5.18 (1H, d, *J* = 14, HCHPh); 7.33-7.37 (5H, m, $H–C_{Ph}$). ^{13}C NMR spectrum, δ, ppm: -2.5 ($Si(\underline{C}H_3)_3$); 30.6; 50.0; 51.8; 67.5; 128.1; 128.4; 128.6; 139.8; 154.6. Mass spectrum, *m/z* (I_{rel}, %): 204 (8) $[M–91]^+$, 160 (22), 91 (100), 73 (44). Found, %: C 56.66; H 7.44; N 4.45. $C_{14}H_{21}NO_2SSi$. Calculated, %: C 56.91; H 7.16; N 4.74.

2-Trimethylsilyl-1,3-oxazolidines (General procedure). To a freshly prepared solution of compound **2** (8.7 mmol) (obtained from methoxymethyltrimethylsilane and bromine in CCl_4) was added at room temperature anhydrous CH_2Cl_2 (10 ml), the appropriate N-protected β-amino alcohol (8.7 mmol) dissolved in 5 ml of CH_2Cl_2, and DIPEA (1.2 eq). The mixture was stirred overnight, then was treated with *p*-toluenesulfonic acid (0.1 eq) for 90 min. The resulting mixture was washed with water and brine, and the organic phase was dried over Na_2SO_4. Evaporation of the solvent afforded the crude N-protected oxazolidines, which were purified by flash chromatography.

Benzyl 2-(trimethylsilyl)oxazolidine-3-carboxylate (**10**). Petroleum ether/ethyl acetate, 5:1 (52%). ^1H NMR spectrum, δ, ppm (*J*, Hz): 0.07 (9H, s, $SiMe_3$); 3.19-3.34 (1H, m, HCHN); 3.63-3.81 (2H, m, HCHN+HCHO); 4.01-4.12 (1H, m, HCHO); 4.77 (1H, s, $HCSiMe_3$); 5.10-5.16 (2H, m, CH_2Ph); 7.35-7.37 (5H, m, $H–C_{Ph}$). ^{13}C NMR spectrum, δ, ppm: -3.1 ($Si(\underline{C}H_3)_3$); 45.7; 67.0; 67.9; 85.7; 127.9; 128.3; 138.6; 156.5. Mass spectrum, *m/z* (I_{rel}, %): 264 (0.5) $[M–15]^+$, 188 (7), 144 (26); 91 (100), 73 (43). Found, %: C 59.96; H 7.72; N 5.17. $C_{14}H_{21}NO_3Si$. Calculated, %: C 60.18; H 7.58; N 5.01.

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