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USE OF POTASSIUM FLUORIDE IN THE CYCLIZATION OF 3-HETERO-1,5-DIALDEHYDES WITH NITROMETHANE AND ETHYL NITROACETATE

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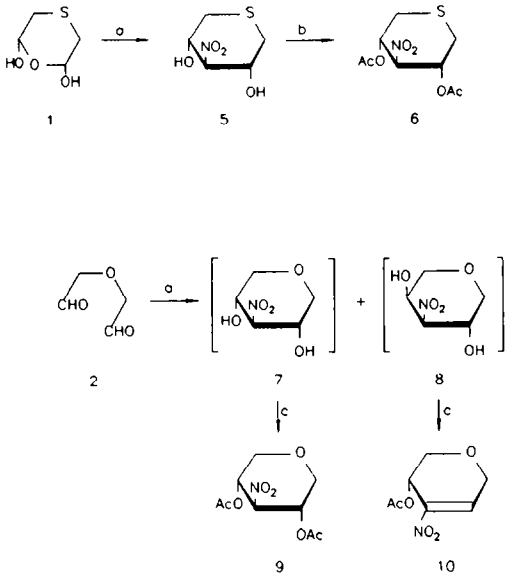
Abstract.-The use of potassium fluoride as catalyst in the cyclization reactions of dialdehydes is described for the first time. This compound is an efficient catalyst in the cyclizations with nitromethane and ethyl nitroacetate. The yields obtained are similar or higher than those reported when other catalysts are used and the stereoselectivity was major when the dialdehyde prepared by periodate oxidation of methyl α-L-rhamnopyranoside was used.

Glycosides of 3-deoxy-3-nitroaldoses are readily available by the cyclization of "sugar dialdehydes"[1-4] with nitromethane. Introduced in 1958 by Baer and Fischer[5], the method has been widely employed and reviewed[6-8]. This reaction has been effected with a large variety of aliphatic, sugar and nucleoside dialdehydes[7,8], and nitroalkanes (nitroethane, nitroethanol, ethyl nitroacetate, 1-nitropropene and phenylnitromethane)[8]. Cyclization of the dialdehyde with nitroalkane in methanol or ethanol is usually effected in the presence of one molar equivalent of sodium methoxide or sodium ethoxide for 1-6 h at 0-25°C. The reaction products may be isolated as *aci*-nitro salts, which in some cases precipitate from the reaction mixture, or to directly deionize the mixture with a cation-exchange resin in the acid form. Aqueous conditions have also been used, employing sodium hydroxide, barium hydroxide, sodium carbonate or potassium carbonate[7,8] as the base but do not seem to offer preparative advantages. In some instances, however, the products formed are dependent on the type of base used.

The aldol condensation of aldehydes and nitroalkanes (the Henry reaction[9,10]) is normally carried out in the presence of bases such as hydroxide or alkoxide, and constitutes an important route to nitro alcohols. These reactions may be readily accomplished by using KF as the basic catalyst[11-13]. 2-Propanol or acetonitrile have been suggested as suitable solvent for such reactions, and the reactions are accelerated by adding a catalytic quantity of 18-crown-6[12]. This fact led us to explore the use of potassium fluoride as catalyst in the cyclization of 3-hetero-1,5-dialdehydes with nitromethane and alkyl nitroacetates using isopropanol or acetonitrile as solvent. We report here the reactions of nitromethane with *cis*-2,6-dihydroxy-1,4-oxathiane (**1**)[14], diglycolaldehyde (**2**)[15], α-(S)-(3-ethoxycarbonyl-2-methylfur-5-yl)diglycolaldehyde (**3**)[16], and (2*R*, 3*R*, 5*S*, 6*S*)-3,5-dihydroxy-6-methyl-2-methoxy-1,4-dioxane (**4**)[17], and the reaction of **1** with ethyl nitroacetate using KF as catalyst.

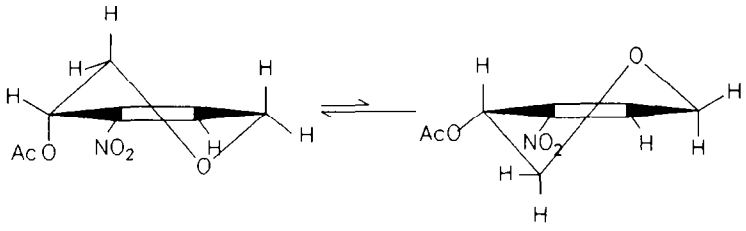


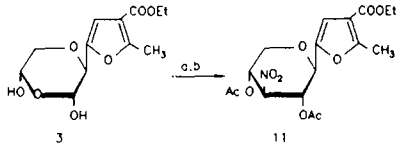
(a) KF-isopropanol-dibenzo 18-crown-6, CH_3NO_2. (b) Ac_2O-$BF_3 \cdot OEt_2$. (c) Ac_2O-AcOH-AcCl.

Seebach *et al.* reported[18] that the reactions of the internal hemialdal **1** and diglycolaldehyde (**2**) with nitromethane and sodium hydroxide in methanol afforded **5** (66%) and **9** (5%, after acetylation), respectively. We found that the cyclization of **1** with nitromethane using potassium fluoride in isopropanol gave **5** in 71% yield. Compound **5** was acetylated (with boron trifluoride catalysis) to give its diacetate **6** (70%).

Cylization of the dialdehyde **2** with nitromethane in similar conditions gave a crude product that was purified by column chromatography. The faster-moving fraction was acetylated with the mixture acetic acid-acetic anhydride-acetyl chloride giving **9** (28%) after purification of crude product by column chromatography on silica-gel. The slower-moving fraction was also acetylated with the same mixture affording the nitro-olefin **10** (23.5%), that could be formed from the diacetyl derivative of **8** by dehydroacetylation. This is supported by the fact that the ^{1}H-NMR spectrum of the slower-moving fraction before the acetylation did not show signals corresponding to olefinic protons. Some dehydroacetylation of methyl 2,4-di-O-acetyl-3,6-dideoxy-3-nitrohexopyranosides have been reported by Baer *et al.*[19]. Compound **10** showed $J_{5,6}$ = 1.4 Hz and $J_{5,6'}$ = 2.4 Hz in agreement[20] with the preferred ^6H_O conformation **10A**. This is also in accordance[20] with the $J_{3,4}$ and $J_{2,5}$ values of ≈0 Hz and 2.3 Hz, respectively. The allylic effect[21] favours this conformer.

The use of KF as catalyst in the cyclization reactions was also applied to the dialdehydes **3** and **4**. The treatment of **3** with nitromethane gave **11** (27.5%), isolated after acetylation of the crude product with boron trifluoride. Compound **11** showed $J_{1,2} + J_{2,3}$ and $J_{3,4} \approx J_{4,5a}$ values of 20.0 Hz and ≈10.3 Hz, respectively,





(a) KF-isopropanol-dibenzo 18-crown-6, CH_3NO_2. (b) Ac_2O-BF_3·OEt_2.

according with an equatorial disposition for the nitro and acetoxy groups in a $^4C_1$(D) preferred conformation.

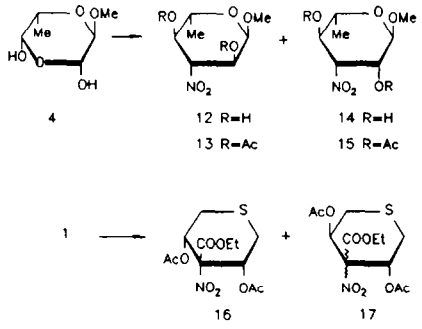
The hemialdal **4** was obtained following the method described by Richardson *et al.*[17c] but a modification was introduced in the work-up. The salts were removed by precipitation with 1,4-dioxane, and the syrup obtained after evaporation was purified by column chromatography giving **4** isolated as a solid. The ^{1}H-NMR. spectroscopic data for this compound are in accordance with a diaxial disposition for the hydroxy groups ($J_{2,3} \approx J_{5,6} \approx 1$ Hz).

Cyclization of the dialdehyde obtained from methyl α-L-rhamnopyranoside with nitromethane and sodium methoxide in methanol was reported[17c,22,23]. Four methyl 3,6-dideoxy-3-nitro-α-L-hexopyranosides with *gluco, manno, talo* and *galacto* configurations were isolated by Baer *et al.*[23]. When **4** was cyclizated with nitromethane using KF as catalyst **12** was isolated by crystallization of the crude reaction mixture. Acetylation of the mother liquors gave a mixture of **13** and **15**. Compound **12, 13** and **15** were characterized by comparison of the physical data with those reported[19,23]. These results show that this reaction is more stereoselective when KF is used as catalyst instead of sodium methoxide.

On the basis of the results described above we were interested to test if KF is also an efficient catalyst in the cyclization of dialdehydes with alkyl nitroacetates.

The reaction of **1** with ethyl nitroacetate using KF as catalyst and acetonitrile as solvent furnished the diacetyl derivatives **16** (7.5%) and **17** (27.2%) after acetylation of the crude product mixture.

Compound **16** is a *meso* form and showed only an ABX system for the hydrogen bonded at the ring carbon atoms. The values for $J_{2e,3}$ and $J_{2a,3}$ of 5.0 Hz and 11.0 Hz, respectively, according with the



diequatorial disposition of the acetoxy groups. The configuration at C-4 in **16** was assigned on the basis of the heteronuclear $J_{COOEt,H}$ (≈ 7.0 Hz) in agreement[24] with an axial disposition for the COOEt group and a diaxial disposition for H-3,5. The axial protons H-2a and H-6a show higher shielding than the corresponding equatorial proton H-2e and H-6e. This could be explained by an anisotropic effect or by deshielding of the axial ethoxycarbonyl group at C-4. This is according with the configuration assigned at C-4.

Compound **17** showed two ABX systems for the hydrogens bonded at the ring carbon atoms. The values for $J_{2a,3a}$, $J_{2e,3a}$, $J_{5e,6a}$, and $J_{5e,6e}$ were 9.4, 5.1, 4.9 and 2.2 Hz, respectively. The configuration at C-4 in **17** could not be assigned on the basis of the heteronuclear $^3J_{COOEt,H}$ values, because accurate data could not be obtained. The chemical shifts values for **16** and **17** (^{1}H- and ^{13}C-NMR) (see Experimental Section) are also in accordance with the configurational assignments.

In summary, the method reported herein provides a convenient method for the cyclization of dialdehydes with nitromethane and ethyl nitroacetate. This method has attractive advantages, including ease of use and stability of potassium fluoride, clean and efficient reactions, and easy work-up of the product mixture. The yields obtained are similar or higher than those reported and the stereoselectivity was major when the dialdehyde **4** was used. Use of this catalyst in cyclizations of dialdehydes with active methylene compounds is presently under active investigation.

EXPERIMENTAL SECTION

Melting points were recorded in a electrothermal apparatus and are uncorrected. Spectral measurements are recorded on Perkin-Elmer 983G (IR), Perkin-Elmer 141 (rotations), and Bruker AM 300 (NMR) instruments. Mass spectra data (m/e) were obtained by chemical ionization mode, using ether as the ionizing gas and a Hewlett Packard 5988A instrument. Optical rotations were measured at room temperature. Column chromatography was performed on Silica Gel Merck (70-230 mesh, ASTM).

Synthesis of (2R, 3R, 5S, 6S)-3,5-dihydroxy-6-methyl-2-methoxy-1,4-dioxane (4)[17].- To a cooled solution of methyl α-L-rhamnopyranoside (3.3 g, 18.14 mmol) in water (35 mL) was portionwise added $NaIO_4$ (8.5

g, 39.7 mmol) for ≈10 min under magnetical stirring. The reaction mixture was kept in the dark 1 h, and then $NaHCO_3$ (1.55 g, 18.4 mmol) was added. After the addition of 1,4-dioxane (100 mL) the salts were removed by filtration and the solution evaporated. The treatment with 1,4-dioxane was repeated twice. The crude product was purified by column chromatography (ether-hexane, 5:1) giving **4** (2.5 g, 82%), mp 95-97°C; $[\alpha]_D$ -164 (c 1, H_2O) (lit.[17a] mp 101-102°C; $[\alpha]_D$ -143°). IR(KBr) 3375, 3260, 1152, 1098, 1035 cm^{-1}. NMR data ($(CD_3)_2SO$): ^{1}H-, δ 6.46 (d, 1H, $J_{3,OH}$= 4.5 Hz, OH-C3; exchangeable with D_2O), 6.34 (d, 1H, $J_{5,OH}$= 7.4 Hz, OH-C5; exchangeable with D_2O), 4.64 (d, 1H, $J_{3,OH}$= 4.5 and $J_{2,3}$≈ 0 Hz, H-3), 4.57 (d, 1H, $J_{5,OH}$= 7.4 and $J_{5,6}$≈ 0 Hz, H-5), 4.08 (s, 1H, H-2), 3.43 (m, 1H, H-6), 3.14 (s, 1H, H-2), 3.43 (m, 1H, H-6), 3.14 (s, 3H, MeO), and 0.94 (d, 3H, J= 6.4 Hz, Me); ^{13}C-: δ 97.2 (C-2), 91.1 (C-3,5), 66.5 (C-6), 53.8 (MeO), and 16.3 (Me). (Anal. Calcd for $C_6H_{12}O_5$: C, 43.9; H, 7.37. Found: C, 44.1; H, 7.25).

Reaction of nitromethane with 1-4. General Procedure.- To a solution of dialdehyde in isopropanol was added potassium fluoride (0.1 equiv), nitromethane (3.6 equiv) and dibenzo 18-crown-6 ether (0.1 equiv). The reaction mixture was stirred at ≈45°C for 3-40 h and then evaporated. The crude product was purified by column chromatography or acetylated. The following amounts and conditions were used:

Starting Compound (g, mmol)	Isopropanol (mL)	Time (h)	Products (g, %)
1 (0.5, 3.8)	10	3.5	**5** (0.47, 71)
2 (a)	26	6	**9** (0.68, 28), **10** (0.43, 23)[b]
3 (0.5, 2.0)	15	6	**11** (0.22, 27)[c]
4 (2.0, 12.0)	70	40	**12** (0.50, 20), **13+15** (1.1, 44)[d]

[a]Prepared in the polymeric state from bis(di-isopropyl acetal)[15] (3.0 g, 9.8 mmol). [b]The crude product was acetylated using acetic acid-acetic anhydride-acetyl chloride. [c]The crude product was acetylated by using acetic anhydride and boron trifluoride as catalyst. [d]1:1 Molar ratio (from ^{1}H-NMR).

(a) With thiodiglycolaldehyde[14] (1).- Column chromatography (ether-hexane 5:1) of the crude product gave *trans,trans*-3,5-dihidroxy-*r*-4-nitrotetrahidrothiopyran **5**, mp 151-152°C (from hexane-ether); IR(KBr) 3406, 1618, 1554, 1178, 1150, 1112, 1076 cm^{-1}. ^{1}H-NMR ($(CD_3)_2SO$): δ 5.90 (d, 2H, J= 5.9 Hz, 2OH, exchangeable D_2O), 4.12 (t, 1H, J≈ 9.8 Hz, H-4), 3.83 (seven peaks, 2H, J= 10, 9.8, 5.9 and 5.1 Hz, H-3,5), 2.53-2.36 (m, 4H, H-2,2',6,6'). (Anal. Calcd for $C_5H_9NO_4S$: C, 33.51; H, 5.06; N, 7.82. Found: C, 33.35; H, 5.27; N, 8.04).

Acetylation of **5** (1.5 g) with acetic anhydride (14 mL) and $BF_3 \cdot OEt_2$[19] (3 drops) gave **6** (70 %), mp 152-154°C (from ethanol) (lit.[18] mp 138°C). The ^{1}H-NMR spectrum was identical to the one reported[18]. ^{13}C-NMR ($CDCl_3$): δ 169.1 (2CO), 90.6 (C-4), 72.1 (C-3,5), 30.1 (C-2,6), and 20.6 (2MeCO).

(b) With diglycolaldehyde (2).- Column chromatography (ether-hexane 2:1) gave two fractions that were separately acetylated. The fast-moving fraction (0.51g) was treated with acetic acid-acetic anhydride-acetyl chloride (1:1:2 mL) at room temperature for 16 h. *trans,trans*-3,5-Diacetoxy-*r*-4-nitrotetrahydropyran **9** was obtained after standard work-up; mp 123-124°C (from ether-hexane) (lit.[18] 104-105°C). The NMR spectra were identical to those reported[18].

Acetylation of the slow-moving fraction (0.74 g) with the mixture acetic acid-acetic anhydride-acetyl chloride (2:2:4 mL) at room temperature for 16 h gave 5-acetoxy-4-nitro-5,6-dihidro-2H-pyran (**10**) isolated as a syrup. IR (film) 3082, 1738, 1671, 1556, 1523 cm^{-1}. NMR data ($CDCl_3$): ^{1}H-, δ 7.57 (dd, 1H, $J_{2,3}$= 3.8 and $J_{2',3}$= 1.8 Hz, H-3), 5.83 (m, 1H, H-5), 4.60 (dd, 1H, $J_{2,2'}$= 19.5 and $J_{2,3}$= 3.8 Hz, H-2), 4.30 (dt, 1H, $J_{2,2'}$= 19.5, $J_{2',3}$= 1.8 and $J_{2',5}$= 2.3 Hz, H-2'), 4.15 (dd, 1H, $J_{6,6'}$= 13.1 and $J_{5,6}$= 1.4 Hz, H-6), 3.65 (dd, 1H, $J_{6,6'}$= 13.1 and $J_{5,6'}$= 2.4 Hz, H-6'), and 2.06 (s, 3H, Ac); ^{13}C-: δ 170.0 (CO), 137.6 (C-3), 68.3, 64.1, 62.2 (C-2,5,6), and 20.7 (MeCO). MS m/e: 188 ($M^{+\cdot}$+1), 187 ($M^{+\cdot}$), 145 ($M^{+\cdot}$-C_2H_3O), 127 ($M^{+\cdot}$-$C_2H_4O_2$).

(c) With α-(S)-(3-ethoxycarbonyl-2-methylfur-5-yl)-diglycolaldehyde (3)[16].- The crude product was conventionally acetylated with acetic anhydride (4 mL) and BF_3-etherate (3 drops) giving 5-(2,4-di-O-acetyl-3-deoxy-3-nitro-ß-D-*xylo*-pentopyranosyl)-3-ethoxycarbonyl-2-methylfuran (**11**), mp 129-130°C (from ether-hexane); $[\alpha]_D$ -19° (c 1, Cl_3CH). IR(KBr) 1755, 1706, 1562, 1296, 1220, 1082 cm^{-1}. NMR data ($CDCl_3$): ^{1}H-, δ 6.65 (s, 1H, H-furan), 5.68 (pseudo-t, 1H, $J_{1,2}+J_{2,3}$= 20.0 Hz, H-2), 5.50 (dpseudo-t, 1H, $J_{3,4}\approx J_{4,5a}\approx$ 10.3 and $J_{4,5e}$= 5.6 Hz, H-4), 4.84 (pseudo-t, 1H, $J_{2,3}+J_{3,4}$= 20.5 Hz, H-3), 4.35-4.30 (m, 2H, H-1,5e), 4.25 (q, 2H, J= 7.2 Hz, OCH_2CH_3), 3.37 (pseudo-t, 1H, $J_{4,5}+J_{5a,5e}$= 21.8 Hz, H-5a), 2.55 (s, 3H, Me-furan), 2.05, 1.91 (2s, 6H, 2Ac), and 1.16 (t, 3H, J= 7.2 Hz, OCH_2CH_3); ^{13}C-: δ 169.0 (C-3), 111.5 (C-4), 88.8 (C'-3), 77.6, 68.7, 68.0 (C'-1,2,4), 66.6 (C'-5), 60.4 (OCH_2CH_3), 20.5, 20.3 (2MeCO), and 14.4, 13.9 (Me-furan, CH_3CH_2O). (Anal. Calcd. for $C_{17}H_{21}NO_{10}$: C, 51.13; H, 5.30; N, 3.52. Found: C, 51.40; H, 5.27; N, 3.74).

(d) With (2R, 3R, 5S, 6S)-3,5-dihydroxy-6-methyl-2-methoxy-1,4-dioxane (4).- Column chromatography (ether-hexane 1:1) of the crude product gave a mixture of methyl 3,6-dideoxy-3-nitro-α-L-*gluco*- (**12**) and α-L-*manno*-hexopyranosides (**14**). Treatment of this mixture with chloroform gave pure **12**, mp, $[\alpha]_D$ and spectroscopic data were identical to those reported[23]. The mother liquors were formed by a mixture of **14** and **15** in a ≈1:1 ratio (deduced from ^{1}H-NMR). Acetylation in the same conditions to those reported[19] gave a mixture of **13** and **15** in a ≈1:1 ratio that showed signals in ^{1}H-NMR identical with those described[19] for these compounds.

Reaction of ethyl nitroacetate with 1.- To a solution of **1** (0.5 g, 5.7 mmol) in acetonitrile (25 mL) were added KF (30 mg), ethyl nitroacetate (0.5 g) and dibenzo 18-crown-6 ether (0.1 equiv). The reaction mixture was stirred at room temperature for 4 h, and then evaporated. The crude product was dissolved in water (20 mL) and extracted with ethyl acetate (3 x 100 mL). The organic phase was dried, filtered and concentred to give a crude product that was acetylated with the mixture acetic acid-acetic anhydride-acetyl chloride (3:3:8 mL) at room temperature for 16 h. After standard work-up and column chromatography (ether-

hexane 1:4) two fractions were isolated. The fast-moving one was constituted by *trans*-3,5-diacetoxy-4-ethoxycarbonyl-4-nitrotetrahydrothiopyran (**17**) (0.47 g, 27%), mp 71-72°C (from ether-hexane). IR(KBr) 1757, 1735, 1561 cm^{-1}. NMR data ($CDCl_3$): ^{1}H-, δ 5.85 (dd, 1H, 1H, $J_{2a,3}$= 9.4 and $J_{2e,3}$= 5.1 Hz, H-3), 5.78 (dd, 1H, $J_{5,6a}$= 4.9 and $J_{5,6e}$ 2.2 Hz, H-5), 4.40-4.14 (m, 2H, $OC\underline{H}_2CH_3$), 3.47 (dd, 1H, $J_{6a,6e}$= 14.8 Hz and $J_{5,6e}$= 2.2 Hz, H-6e), 2.90-2.74 (m, 3H, H-2a,2e,6a), 1.99, 1.98 (2s, 6H, 2Ac), and 1.23 (t, 3H, J= 7.1 Hz, $OCH_2C\underline{H}_3$); ^{13}C-, δ 168.6 (2Me$\underline{C}$O), 162.7 ($\underline{C}$OOEt), 93.2 (C-4), 70.7, 68.9 (C-3,5), 63.5 ($O\underline{C}H_2CH_3$), 28.9, 27.7 (C-2,6), 20.6 (2$\underline{Me}$CO) and 13.8 ($\underline{C}H_3CH_2O$). (Anal. Calcd for $C_{12}H_{17}NO_6S$: C, 47.52; H, 5.65; N, 4.62. Found: C, 47.40; H, 5.75; N, 4.78).

The slow-moving fraction corresponded to *trans,trans*-3,5-diacetoxy-4-ethoxycarbonyl-*r*-4-nitrotetrahydrothiopyran (**16**) (0.13 g, 7%), mp 113-114°C (from ether-hexane). IR (KBr) 1750, 1561, 1376, 1218 y 1032 cm^{-1}. NMR data ($CDCl_3$): ^{1}H-, δ 5.63 (dd, 2H, $J_{2a,3}$= 11.0 and $J_{2e,3}$= 5.0 Hz, H-3,5), 4.40 (c, 2H, J= 7.1 Hz, $OC\underline{H}_2CH_3$), 3.15 (dd, 2H, $J_{2a,2e}$= 13.6 and $J_{2a,3}$= 11.0 Hz, H-2a,6a), 2.85 (ddd, 2H, $J_{2a,2e}$= 13.6, $J_{2e,3}$ 5.0 and $J_{2e,6e}$= 1.2 Hz, H-2e,6e), 2.05 (s, 6H, 2Ac) and 1.33 (t, 3H, J= 7.1 Hz, $OCH_2C\underline{H}_3$); ^{13}C-, δ 168.9 (2CO), 162.3 ($\underline{C}$OOEt), 94.2 (C-4), 72.5 (C-3,5), 63.4 ($O\underline{C}H_2CH_3$), 28.5 (C-2,6), 20.7 (2$\underline{Me}$CO) and 14.2 ($\underline{C}H_3CH_2O$). (Anal. Calcd for $C_{12}H_{17}NO_6S$: C, 47.52; H, 5.65; N, 4.62. Found: C, 47.22; H, 5.37; N, 4.76).

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