Synthesis of β-formyl-2,5-dialkoxytetrahydrofurans and their reaction with 3-amino-1,2,4-triazole

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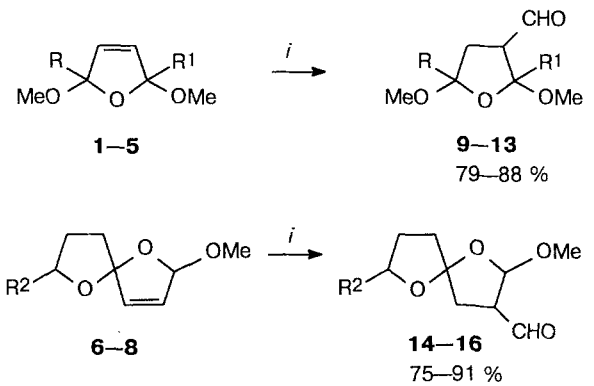
New β-formyl-2,5-dialkoxytetrahydrofurans were synthesized by hydroformylation of the corresponding 2,5-dihydrofurans. The aldehydes obtained react with 3-amino-1,2,4-triazole to give 6-(2-oxopropyl)-1,2,4-triazolo[1,5-*a*]pyrimidines.

Key words: tetrahydrofurans, hydroformylation, azolopyrimidines.

Hydroformylation of dihydrofurans is a convenient method for synthesizing aldehydes of the tetrahydrofuran series.[1]

We hydroformylated α-substituted 2,5-dimethoxy-2,5-dihydrofurans **1—5** and their spirocyclic analogs, namely, 7-substituted 2-methoxy-1,6-dioxaspiro[4,4]non-3-enes **6—8**, in the presence of homogeneous rhodium-containing catalysts:



R^1 = H; R = Me (**1**, **9**), CH_2OH (**2**, **10**), CH_2OMe (**3**, **11**), CH_2OCMe (**4**, **12**);

R = R^1 = Me (**5**, **13**); R^2 = H (**6**, **14**), Me (**7**, **15**), Ph (**8**, **16**)

i. CO, H_2, Rh-catalyst .

The starting 2,5-dihydrofurans **1—8** were obtained by methoxylating the corresponding furans.[2,3] Under Clauson-Kaas reaction conditions, 2-(3-hydroxypropyl)-furans yield 2-methoxy-1,6-dioxaspiro[4,4]non-3-enes **6—8** through intramolecular alkoxylation-cyclization.

Hydroformylation of 2,5-dihydrofurans was carried out in benzene in the presence of rhodium complexes as catalysts, namely, tris-triphenylphosphinehydridocarbonylrhodium and acetylacetonatocarbonylrhodium modified by organophosphorus ligands.

To find the optimum conditions for synthesizing aldehydes **9—16**, we performed the hydroformylation of a model substrate, namely, 2-methyl-2,5-dimethoxy-2,5-dihydrofuran (**1**). The reaction products were analyzed by GLC.

The results obtained on hydroformylation of compound **1** in the presence of $HRh(CO)(PPh_3)_3$ indicate that the maximum yield of compound **9** is attained in 3 h under the following conditions: the ratio Rh : substrate = 1 : 700; 80 °C; pressure of the synthesis gas (CO : H_2 = 1 : 1) 10 MPa.

The hydroformylation of compound **1** in the presence of $Rhacac(CO)_2$ modified by organophosphorus ligands was carried out with the ratio Rh : substrate = 1 : 700, at 80 °C, and at a pressure of 10 MPa, *i.e.*, under conditions that were optimum for $HRh(CO)(PPh_3)_3$. We studied the effect of the nature and concentration of a modifier (**L**) on the yield of compound **9**. Triphenylphosphine, triphenylphosphite, and 1,2-bis-diphenylphosphinoethane were tested as modifiers. The following rule was found for all three catalytic systems: the yield of **9** is proportional to the concentration of a modifying component up to a threshold, which is at the ratio **L** : Rh = 6 : 1. Further increase in the concentration of **L** does not lead to any significant increase in the yield. Under the above conditions, the system $Rhacac(CO)_2$ + 6 PPh_3 makes it possible to obtain compound **9** in almost quantitative yields. The results for the other two modifiers were worse: the yields of **9** were no more than 50 %.

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The preparative syntheses of aldehydes **9—12** and **14—16** were carried out for 3 h in the presence of the catalyst $HRh(CO)(PPh_3)_3$ or $Rhacac(CO)_2$ + 6 PPh_3, at the ratio Rh : substrate = 1 : 700, at 80 °C, and at a synthesis gas pressure of 10 MPa. The yields were 75—91 %.

The IR spectra of these compounds contain a strong absorption band in the region of 1730 cm^{-1}, which corresponds to the formyl group, and a broad band around 3500 cm^{-1}. The latter is obviously due to a hydroxy group in the dimer formed as a result of aldol autocondensation. Furthermore, the spectrum of compound **12** contains a strong band at 1730 cm^{-1} caused by absorption of the ester carbonyl, while the spectrum of compound **11** contains an absorption band of the phenyl group at 1615 cm^{-1}.

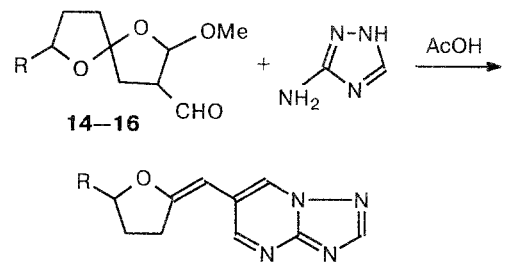
The low field regions of the ^1H NMR spectra of aldehydes **9—16** contain several signals of the formyl group protons at 9.5—9.8 ppm, which are due to the presence of diastereomers. The spectrum also contains characteristic signals of the acetal protons with chemical shifts of 3.3—3.6 ppm. The signal of the proton located in the geminal position relative to the formyl group appears at 3.3—3.4 ppm.

We believe that the regioselectivity of the hydroformylation of asymmetric 2,5-dihydrofurans **1—4** and **6—8** can be explained by migration of the double bond in the substrate molecules in the presence of the rhodium complex and by steric effects:

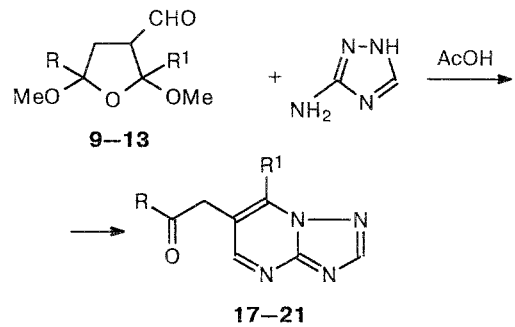
i. Rh-catalyst

Isomerization of 2,5-dihydrofurans into the 2,3-isomers in the presence of transition metal complexes has been reported previously.[4,5] As a result, the attack of the catalytic complex at the ring position that is the most distant from the quaternary carbon atom becomes favorable. We observed the pure effect of steric hindrance in the case of hydroformylation of compound **5**. Since the molecule is symmetric, migration of the double bond is impossible. Hence, steric hindrance should cause a decrease in the reaction rate, which was indeed observed experimentally. Under the above conditions ($Rhacac(CO)_2$: **5** = 1 : 700, 80 °C, 10 MPa), the degree of conversion was 65 % over 4 h. To attain a good yield of aldehyde **13**, we had to increase the catalyst content (1 : 300) or increase the temperature (120 °C).

Aldehydes **9—16** are analogs of 1,3-dicarbonyl compounds, which opens up good prospects for their use for synthesizing heterocycles. We have previously reported the synthesis of 6-(2-oxopropyl)-1,2,4-triazolo-[1,5-*a*]pyrimidine by the reaction of compound **9** with 3-amino-1,2,4-triazole.[6] Similar condensation of spirocyclic aldehydes **14—16** yields 2-(1,2,4-triazolo-[1,5-*a*]pyrimidin-6-yl)-methylenetetrahydrofurans:[7]



In a continuation of these studies, we suggest a method for synthesizing functionally 6-substituted 1,2,4-triazolo[1,5-*a*]pyrimidines by treatment of β-formyl-2,5-dimethoxytetrahydrofurans **9—13** with 3-amino-1,2,4-triazole.



R^1 = H; R = Me (**9, 17**), CH_2OH (**10, 18**), CH_2OCH_3 (**11, 19**), CH_2OCOCH_3 (**12, 20**); R^1 = R = Me (**13, 21**)

The reaction was carried out by refluxing equimolar amounts of the starting compounds for 1 h in glacial acetic acid. Compounds **17—21** were isolated in 50—62 % yields.

The structures of the compounds obtained were determined using ^1H, ^{13}C, and ^{15}N NMR spectra of their solutions. The chemical shifts in the ^1H and ^{13}C spectra are in agreement with data reported for 1,2,4-triazolo[1,5-*a*]pyrimidines[8,9] (see Experimental and Table 1). The chemical shifts in the ^{15}N spectra and the $^{15}N—^1H$ coupling constants are presented in Table 2. Similar chemical shifts have been reported in Ref. 8, and the geminal and vicinal $^{15}N—^1H$ coupling constants have been given in Refs. 8 and 10. The presence of a substituent at position 7 of compound **21** is supported by the vicinal coupling constant, $^3J_{N(8),CH}$ = 2.5 Hz. A corresponding coupling constant of similar magnitude has been reported for 1,5-dimethylpyrazoles.[11]

The electron spectra of compounds **17—21** contain two intense absorption maxima in the regions of 213—217 nm (ε 15000—23400) and 270—286 nm (ε 2660—6200). Such a spectrum is typical of alkyl-substituted 1,2,4-triazolo[1,5-*a*]pyrimidines.[12]

Table 1. Physicochemical and spectral characteristics of β-formyl-2,5-dimethoxytetrahydrofurans **9—13**

Compound	Yield (%)	B.p./°C (*p*/Torr)	n_D^{20}	Molecular formula	Found / Calculated (%) C	H	MS M^+ (*m*/*z*)	^{1}H NMR ($CDCl_3$), δ (*J*/Hz)
9	89	76—78 (5)	1.4490	$C_8H_{14}O_4$	55.21 / 55.16	8.02 / 8.10	174	9.6—9.8 (set of s, 1 H, CHO); 5.25 (m, 1 H, 5-CH); 3.3—3.6 (set of s, 6 H, OMe); 3.35 (m, 1 H, 4-CH); 2.3—2.4 (m, 2 H, 3-CH_2); 1.2—1.6 (set of s, 3 H, Me)
10	82	105—110 (2)	1.4700	$C_8H_{14}O_5$	50.47 / 50.52	7.49 / 7.42	190	9.6—9.8 (set of s, 1 H, CHO); 5.25 (m, 1 H, 5-CH); 3.6—3.8 (set of s, 2 H, $\underline{CH_2}OH$); 3.3—3.6 (set of s, 6 H, OMe); 3.4 (m, 1 H, 4-CH); 2.7 (br.s, 1 H, OH); 2.3—2.4 (m, 2 H, 3-CH_2)
11	88	90—93 (2)	1.4482	$C_9H_{16}O_5$	52.85 / 52.93	7.96 / 7.90	204	9.5—9.7 (set of s, 1 H, CHO); 5.30 (m, 1 H, 5-CH); 3.2—3.7 (m, 12 H, 4-CH, OMe, CH_2OMe); 2.3—2.4 (m, 2 H, 3-CH_2)
12	83	110—112 (5)	1.4530	$C_{10}H_{16}O_6$	51.72 / 51.72	6.89 / 6.94	232	9.5—9.7 (set of s, 1 H, CHO); 5.3 (m, 1 H, 5-CH); 4.0—4.2 (m, 2 H, $\underline{CH_2}$OAc); 3.3—3.6 (set of s, 6 H, OMe); 3.3 (m, 1 H, 4-CH); 2.3—2.4 (m, 2 H, 3-CH_2); 1.9 (s, 3 H, MeCO)
13	82	46—48 (1)	1.4400	$C_8H_{16}O_4$	54.59 / 54.53	9.07 / 9.15	188	9.6—9.8 (set of s, 1 H, CHO); 3.2—3.4 (set of s, 6 H, OMe); 3,3 (m, 1 H, 3-CH); 2.2—2.3 (m, 2 H, 4-CH_2); 1.3—1.6 (set of s, 6 H, Me)

Table 2. Physicochemical and spectral characteristics of 1,2,4-triazolo[1,5-*a*]pyrimidines **17—21**

Compound	Yield (%)	M.p./°C (solvent)	UV λ/nm (ε)	MS M^+ (*m*/*z*)	Molecular formula	Found / Calculated (%) C	H	N	^{1}H NMR ($CDCl_3$), δ (*J*/Hz)
17	58	155 ethanol	214 (21000) 286 (4500)	176	$C_8H_8N_4O$	54.59 / 54.54	4.52 / 4.58	31.83 / 31.80	9.18 (d, *J* = 2.4, 1 H, 7-H); 8.73 (d, *J* = 2.4, 1 H, 5-H); 8.58 (s, 1 H, 2-H); 4.03 (s, 2 H, CH_2CO); 2.28 (s, 3 H, Me)
18	50	128—130 ethanol	217 (15100) 210 (6200)	192	$C_8H_8N_4O_2$	50.09 / 50.00	4.12 / 4.20	29.09 / 29.15	9.12 (d, *J* = 2.3, 1 H, 7-H); 8.77 (d, *J* =2.3, 1 H, 5-H); 8.60 (s, 1 H, 2-H); 4.02 (s, 2 H, CH_2CO); 5.40 (br.s, 1 H, OH); 4.28 (s, 2 H, CH_2)
19	62	85—87 benzene	213 (23400) 274 (4430)	206	$C_9H_{10}N_4O_2$	52.49 / 52.42	4.81 / 4.89	27.08 / 27.17	9.18 (d, *J* = 2.4, 1 H, 7-H); 8.73 (d, *J* = 2.4, 1 H, 5-H); 8.58 (s, 1 H, 2-H); 4.00 (s, 2 H, CH_2CO); 4.11 (s, 2 H, CH_2O); 3.44 (s, 3 H, Me)
20	60	83—85 benzene	214 (15000) 278 (2660)	234	$C_{10}H_{10}N_4O_3$	58.21 / 58.25	4.93 / 4.89	13.63 / 13.59	9.22 (d, *J* = 2.3, 1 H, 7-H); 8.74 (d, *J* = 2.3, 1 H, 5-H); 8.60 (s, 1 H, 2-H); 4.08 (s, 2 H, CH_2CO); 4.96 (s, 2 H, CH_2OAc); 2.10 (s, 3 H, Me)
21	60	146—148 ether : ethyl acetate = 1 : 1	214 (21000) 286 (4500)	190	$C_9H_{10}N_4O$	56.89 / 56.83	5.33 / 5.30	29.40 / 29.46	8.63 (s, 1 H, 5-H); 8.58 (s, 1 H, 2-H); 4.13 (s, 2 H, CH_2CO); 2.28 (s, 3 H, Me); 2.70 (s, 3 H, Me)

Table 3. Chemical shifts in ^{13}C NMR spectra and $^{13}C,^{1}H$ coupling constants for 1,2,4-triazolo[1,5-*a*]pyrimidines **17—21** (DMSO-d_6 as the solvent)

Compound	δ, *J*/Hz								
	C-2	C-3a	C-5	C-6	C-7	CH_2-CO	C=O	Other C atoms	
17	155.56 d ^1J = 207.6	153.84 ddd $^3J_{H(2)}$ = 10.0 $^3J_{H(5)}$ = 14.2 $^3J_{H(7)}$ = 3.2	157.42 ddt ^1J = 185.1 $^3J_{H(7)}$ = 5.6 $^3J_{CH_2}$ = 3.6	118.37 dt $^3J_{H(5)}$ = 7.7 $^2J_{CH_2}$ = 6.1	136.15 ddt ^1J = 190.8 $^3J_{H(5)}$ = 5.6 $^3J_{CH2}$ = 5.7	42.44 t ^1J = 130.2	204.27 tq $^2J_{CH_2}$ = 6.3 $^3J_{CH_3}$ = 5.7	29.33 q ^1J = 127.7	
18	155.60 d ^1J = 207.7	153.86 ddd $^3J_{H(2)}$ = 10.1 $^3J_{H(5)}$ = 14.9 $^3J_{H(7)}$ = 3.2	157.47 ddt ^1J = 185.4 $^3J_{H(7)}$ = 5.7 $^3J_{CH_2}$ = 5.0	118.12 ddt $^3J_{H(5)}$ = 8.1 $^3J_{H(7)}$ = 1.6 $^2J_{CH_2}$ = 6.0	136.25 ddt ^1J = 191.0 $^3J_{H(5)}$ = 5.6 $^3J_{CH2}$ = 5.8	38.04 t ^1J = 129.0	207.51 tt $^2J_{CH_2}$ = 6.0 $^2J_{CH_2O}$ = 3.3	67.55 t ^1J = 141.1	
19	155.68 d ^1J = 207.7	153.87 ddd $^3J_{H(2)}$ = 10.2 $^3J_{H(5)}$ = 14.7 $^3J_{H(7)}$ = 3.2	157.53 ddt ^1J = 185.6 $^3J_{H(7)}$ = 5.5 $^3J_{CH_2}$ = 4.0	117.78 dt $^2J_{H(5)}$ = 7.8 $^2J_{CH_2}$ = 6.1	136.42 ddt ^1J = 191.0 $^3J_{H(5)}$ = 6.0 $^3J_{CH2}$ = 5.8	38.40 tt ^1J = 129.6 $^3J_{CH2}$ = 2.8	204.9 tt $^2J_{CH_2}$ = 6.1 $^2J_{CH_2O}$ = 3.0	58.61 ^1J = 141.7 ^3J = 4.4	76.67 tq ^1J = 146.7 ^3J = 4.9
20	155.83 d ^1J = 207.8	153.92 ddd $^3J_{H(2)}$ = 9.9 $^3J_{H(5)}$ = 14.6 $^3J_{H(7)}$ = 3.5	157.45 ddt ^1J = 185.8 $^3J_{H(7)}$ = 5.8 $^3J_{CH_2}$ = 5.2	117.46 dt $^3J_{H(5)}$ = 8.0 $^2J_{CH_2}$ = 6.0	136.56 ddt ^1J = 191.1 $^3J_{H(5)}$ = 5.6 $^3J_{CH2}$ = 5.8	3830 t ^1J = 129.7	200.95 tt $^2J_{CH_2}$ = 6.9 $^2J_{CH_2O}$ = 4.4	20.10 q ^1J = 139.7 169.8 qunit ^2J = 6.9	67.78 t ^1J = 147.8 ^3J = 4.4
21	154.95 d ^1J = 207.	153.84 ddd $^3J_{H(2)}$ = 9.8 $^3J_{H(5)}$ = 13.8	156.34 dt ^1J = 183.6 $^3J_{H(7)}$ = 5.7	116.23 dq $^2J_{H(5)}$ = 7.7 $^2J_{CH_2}$ = 6.1 $^3J_{CH_3}$ = 5.8	146.72 dq ^1J = 190.8 $^3J_{CH_2}$ = 5.7 $^3J_{CH_3}$ = 6.1	42.04 t ^1J = 128.6	204.27 tq $^2J_{CH2}$ = 6.3 $^2J_{CH3}$ = 5.7	13.62 q ^1J = 131.0	29.17 q ^1J = 127.6

Table 4. Chemical shifts in ^{15}N NMR spectra and $^{15}N,^{1}H$ coupling constants for 1,2,4-triazolo[1,5-*a*]pyrimidines **17—21** (DMSO-d_6 as the solvent)

Compound	δ, *J*/Hz			
	N(1) $^2J_{N,H(2)}$	N(3) $^2J_{N,H(2)}$	N(4) $^2J_{N,H(5)}$	N(8) $^3J_{N,H(2)}$
17	−105.62 d (15.7)	−150.11 d (12.7)	−104.14 d (11.8)	−154.33 d (5.4)
18	−105.89 d (15.7)	−150.47 d (13.4)	−104.46 d (11.8)	−154.31 d (6.1)
19	−105.74 d (15.6)	−150.25 d (12.8)	−104.32 d (11.7)	−154.78 d (6.4)
20	−105.76 d (15.0)	−150.30 d (12.0)	−104.36 d (11.7)	−154.30 d (5.8)
21	−111.69 d (16.1)	−149.77 d (13.0)	−109.17 d (11.4)	−151.23 dq (5.6, 2.5)*

* $^3J_{N,H(8),CH_3}$ = 2.5 Hz

Experimental

^1H, ^{13}C, and ^{15}N NMR spectra were recorded on Bruker AC-200P and Bruker AM-300 spectrometers with working frequencies of 300.13, 75.47, and 30.42 MHz, respectively. The ^1H and ^{13}C chemical shifts were measured to within ±0.003 ppm relative to Me_4Si as the internal standard, and the ^{15}N shifts were measured to within ±0.05 ppm using $CH_3—^{15}NO_2$ as the external standard (the high-field ^{15}N chemical shifts are given with the "−" sign in the δ scale). The accuracy of measuring the $^{13}C—^1H$ and $^{15}N—^1H$ coupling constants ranged from 0.5 to 0.1 Hz, depending on the purpose of a particular experiment. The ^{13}C spectra were recorded with proton decoupling (the *gated decoupling* mode). The ^{13}C and ^{15}N spectra were recorded by selective transfer of polarization (STP) from one proton or a group of protons and by STP with simultaneous selective suppression of the other proton or group of protons, which permits the assignment of all far $^{13}C—^1H$ and $^{15}N—^1H$ coupling constants in these systems.[13] IR spectra were recorded on a UR-20 spectrophotometer in thin films on KBr. UV spectra of alcoholic solutions were obtained on a Specord UV-VIS spectrophotometer. Mass spectra were obtained on a Varian CH-6 MAT spectrometer with direct insertion of samples into the ionization chamber.

GLC was performed on an LKhM-8MD chromatograph with a catharometer, a stainless steel column 3×2500 mm, fixed phase 5 % silicone SE-30 on Chromaton N-AW; helium as the carrier gas; evaporator temperature 250 °C. The temperature of the column was varied from 100 to 150 °C.

β-Formyl-2,5-dimethoxytetrahydrofurans (9—16). The starting dihydrofuran (30 mL), $HRh(CO)(PPh_3)_3$ (ratio Rh : substrate = 1 : 700) or $Rhacac(CO)_2$ and PPh_3 (ratio Rh : PPh_3 : substrate = 1 : 6 : 700), and dry benzene (70 mL) were charged into a rotating steel autoclave (volume 250 mL). The autoclave was purged with CO (pressure 1—1.5 MPa), then CO (up to a pressure of 5 MPa) and H_2 (10 MPa) were fed into the autoclave. The reaction was carried out for 3 h at 80 °C (or 120 °C in the case of

compound **13**). The autoclave was then cooled, the reaction mixture was discharged, the solvent was evaporated, and the residue was distilled (compound **16** was isolated chromatographically on a column with silica gel 40/100 using chloroform : ether, 1 : 1, as the eluent).

The yields and characteristics of compounds **9—13** are presented in Table 1. The characteristics of 3-formyl-2-methoxy-1,6-dioxaspiro[4.4]nonanes **14—16** have been reported previously.[7]

6-(2-Oxopropyl)-1,2,4-triazolo[1,5-*a*]pyrimidines (17—21). β-Formyl-2,5-dimethoxytetrahydrofuran **9—13** (0.01 mol) and 3-amino-1,2,4-triazole (0.01 mol) were dissolved in glacial acetic acid (15 mL) and the solution was refluxed for 1 h. The reaction mixture was cooled, concentrated *in vacuo*, and extracted with benzene (50 mL). The extract was evaporated to dryness, and the residue was recrystallized from a suitable solvent.

The yields and characteristics of compounds **17—21** are presented in Tables 2—4.

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