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REGIOSELECTIVITY IN THE SCHMIDT REACTION: FIRST SYNTHESIS OF PYRANO[3,2-*b*]AZEPINES[#]

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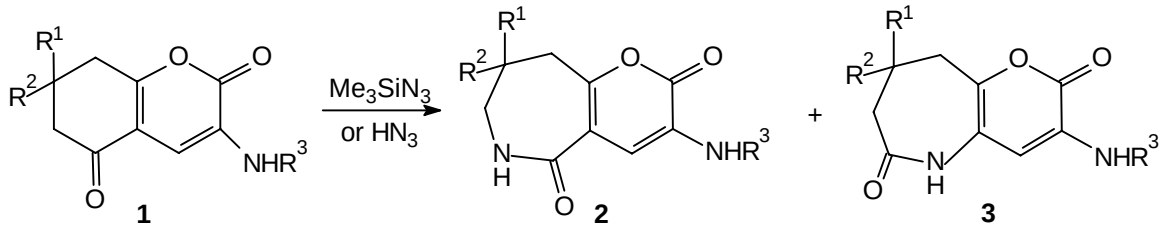
Abstract – The Schmidt reaction of 5,6,7,8-tetrahydro-2*H*-1-benzopyran-2-ones (**1**) has been investigated. Derivatives of pyrano[3,2-*c*]azepines (**2**) and isomeric pyrano[3,2-*b*]azepines (**3**) were isolated by the application of trimethylsilyl azide or sodium azide in a methylene chloride or a chloroform solution in the presence of sulfuric acid. At low temperature products (**2**) were almost sole products, while at higher temperature derivatives (**3**) were also isolated in reasonable yields. Derivatives of pyrano[3,2-*c*]pyridines (**5**) can be prepared from cyclopenta-[*b*]pyran-2,5-diones (**4**) employing the same method.

The Schmidt[1] and related Beckmann[2] reactions have often been used for the synthesis of fused lactams. In some cases these reactions give the same products, but there are also examples where they complement each other leading to isomeric products as a result of the different regiochemistry of nitrogen insertion.[1c,d,3] Recently, we described a synthesis of a new heterocyclic system (pyrano[3,2-*c*]azepine)[4] from 5,6,7,8-tetrahydro-2*H*-1-benzopyran-2,5-diones by the application of the Schmidt reaction with a large excess of hydrazoic acid.[5] We also used such transformation for the synthesis of some 1*H*-pyrido[3,2-*c*]azepines, which have been isolated as sole products.[6] Some 3-aminopyrano[3,2-*c*]azepines[7] have been applied in a new transformation as synthons for the first synthesis of pyridazino[4,3-*c*]azepines.[8] This disclosure prompted us to prepare the derivatives of another new heterocyclic system, namely, pyrano[3,2-*b*]azepine. Previous results have shown that the preparation of 5-hydroxyimino-2*H*-1-benzopyran-2-ones from 2*H*-1-benzopyran-2,5-diones is excluded, because the latter compounds react with some simple nitrogen-containing nucleophiles, including hydroxylamine, first in the pyran-2-one ring giving the corresponding quinoline-2,5-diones and not isomeric 5-imino- or 5-hydrazono-2*H*-1-

[#] *Dedicated to Professor James P. Kutney on the occasion of his 70th birthday.*

benzopyrans.[5,6b,6c,9] On this basis the Beckmann reaction was excluded as an option for the synthesis of pyrano[3,2-*b*]azepines. On the other side, the Schmidt reaction has shown to give isomeric pyrano[3,2-*c*]azepines in high yields.[5] However, we tried to modify the latter reaction by changing reaction conditions and/or reagents to obtain appropriate pyrano[3,2-*b*]azepines in at least reasonable yields. In order to avoid an application of the explosive hydrazoic acid we decided to use trimethylsilyl azide (TMSA)[10a] which had been shown to react with carbonyls in a direct addition under neutral conditions,[10b] in the presence of Lewis acid catalyst[10c,d] or sodium azide/15-crown-5[10d] as well as in a conjugate addition in the presence of a carboxylic acid.[10e]

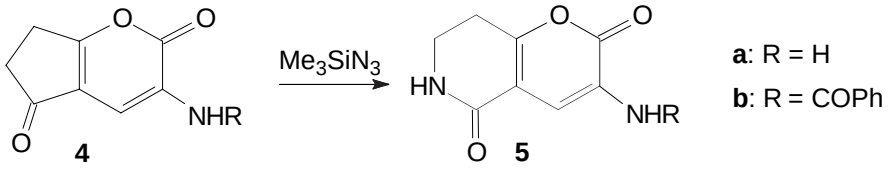
In a preliminary experiment we heated **1c**[5,7] with an excess (5 equivalents) of TMSA for 13 h in a chloroform solution, but no reaction took place and 83% of starting **1c** was recovered. When the same compound (**1c**) was stirred for 5 h at room temperature in a methylene chloride solution with 10 equivalents of TMSA in the presence of 5 equivalents of $BF_3 \times Et_2O$ starting **1c** was again recovered in 96% yield. Similarly, when starting **1b**[7] was stirred at room temperature for 16 h and then refluxed for 5 h in a methylene chloride solution with 4 equivalents of TMSA and 1.2 equivalents of *p*-toluenesulfonic acid no reaction took place and 80% of **1b** was recovered. For this reason we performed reactions of substrates (**1a–f**)[5,7,11a–b] with TMSA and sodium azide in methylene chloride or chloroform solution at different temperatures. So we prepared at temperature around −15 to 0 °C almost isomerically-pure 6,7,8,9-tetrahydropyrano[3,2-*c*]azepine-2,5-diones (**2a–f**), while at temperatures around 35 °C they were accompanied by isomeric 5,7,8,9-tetrahydropyrano[3,2-*b*]azepine-2,6-diones (**3a–f**) (Scheme 1, Table 1). Overall yields of both types of products were high (78–99%).



a: $R^1 = R^2 = R^3 = H$ **d**: $R^1 = R^2 = H$, $R^3 = COPh$
b: $R^1 = R^3 = H$, $R^2 = Me$ **e**: $R^1 = H$, $R^2 = Me$, $R^3 = COPh$
c: $R^1 = R^2 = Me$, $R^3 = H$ **f**: $R^1 = R^2 = Me$, $R^3 = COPh$

Scheme 1

The reaction was extended to cyclopenta[*b*]pyran-2,5-diones (**4a**)[11c] and (**4b**).[11b] Here no temperature dependence of the reaction was observed and derivatives (**5a**) and (**5b**) of 7,8-dihydro-2*H*-pyrano[3,2-*c*]pyridine-2,5(6*H*)-diones were isolated as sole products (Scheme 2, Table 1). The method represents a new approach to 2*H*-pyrano[3,2-*c*]pyridine derivatives.[12]



Scheme 2

Table 1. Reaction Conditions and Yields of Products (**2**, **3** and **5**):

Run	Substrate (**1**) (mmol)	Conditions (azide, solvent, temperature, react. time after azide addition)	products ratio[a] (overall yield, %)
1	**1a** (2)	NaN_3, $CHCl_3$, −15 to 0 °C, 5 h	**2a**/**3a** 10/1 (78)
2	**1a** (2)	NaN_3, $CHCl_3$, 32–35 °C, 2 h	**2a**/**3a** 3.3/1 (85)
3	**1a** (1)	Me_3SiN_3, CH_2Cl_2, 32–35 °C, 2 h	**2a/3a** 4.5/1 (81)
4	**1b** (2)	NaN_3, $CHCl_3$, −15 to 0 °C, 5 h	**2b**/**3b** 38/1 (94)
5	**1b** (1)	Me_3SiN_3, CH_2Cl_2, −15 to 0 °C, 5 h	**2b/3b** 20/1 (96)
6	**1b** (1)	Me_3SiN_3, CH_2Cl_2, 32–35 °C, 2 h	**2b**/**3b** 4.2/1 (99)
7	**1b** (2)	NaN_3, $CHCl_3$, 32–35 °C, 2 h	**2b/3b** 3.2/1 (96)
8	**1c** (1)	Me_3SiN_3, CH_2Cl_2, 32–35 °C, 2 h	**2c/3c** 2.3/1 (83)
9	**1c** (2)	NaN_3, $CHCl_3$, −15 to 0 °C, 5 h	**2c/3c** 17.5/1 (85)
10	**1d** (1)	Me_3SiN_3, CH_2Cl_2, −15 to 0 °C, 5 h	**2d**/**3d** 21/1 (98)
11	**1d** (2)	NaN_3, $CHCl_3$, 32–35 °C, 2 h	**2d**/**3d** 3.9/1 (99)
12	**1e** (1)	Me_3SiN_3, CH_2Cl_2, −15 to 0 °C, 5 h	**2e/3e** 10/1 (92)
13	**1e** (2)	NaN_3, $CHCl_3$, 32–35 °C, 2 h	**2e**/**3e** 4.3/1 (97)
14	**1f** (1)	Me_3SiN_3, CH_2Cl_2, −15 to 0 °C, 5 h	**2f/3f** 18/1 (98)
15	**1f** (2)	NaN_3, $CHCl_3$, −15 to 0 °C, 5 h	**2f/3f** 9/1 (99)
16	**1f** (2)	NaN_3, $CHCl_3$, 32–35 °C, 2 h	**2f/3f/(2c/3c)**[b] 3.1/1 (~98)[c]
17	**4a** (1)	Me_3SiN_3, CH_2Cl_2, rt, 3 h	**5a** (67)
18	**4b** (1)	Me_3SiN_3, CH_2Cl_2, rt, 3 h	**5b** (71)

[a]Product ratio was determined on the basis of ^{1}H NMR spectrum of the crude mixture of isomers. [b]Debenzoylated products were also formed in a small quantity (1–2% each). [c]Yields of debenzoylated products have also been taken into account.

In conclusion, we developed a methodology for the preparation of a novel heterocyclic pyrano[3,2-*b*]-azepine system, isomeric to those we described recently.[5,7,14] The method regulates the regioselectivity of the Schmidt reaction by varying reaction conditions.

EXPERIMENTAL

Melting points were determined on a Kofler micro hot stage, and are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded in DMSO-d_6 with the Bruker Avance DPX 300 spectrometer, using TMS as an internal standard. The coupling constants (*J*) are given in Hz. IR spectra were obtained with a Bio-Rad FTS 3000 MX spectrophotometer. MS spectra were recorded with a VG-Analytical AutoSpec Q instrument. Elemental analyses (C, H, N) were performed with a Perkin Elmer 2400 CHN Analyzer. Thin-layer chromatography was carried out on Fluka silica gel TLC-cards. Merck silica gel 60 PF_{254} containing gypsum was used to prepare chromatotron plates. Methylene chloride was washed with aqueous solution of Na_2CO_3 and distilled over anhydrous $CaCl_2$ before use.

General procedure for preparation of products (2, 3 and 5).

To a mixture of 5-oxo derivative (**1**) in chloroform (40 mL/1 mmol of substrate) and concentrated sulfuric acid (1.5 mL/mmol) on ice-salt bath (temperature of the reaction mixture about −15 to 0 °C) or on water bath at 32–35 °C an excess of sodium azide (6 mmol/1 mmol of substrate) was added portionwise during 1 h; the reaction mixture was then stirred at the same temperature (see Table 1). After the addition of ice and water (*ca*. 80 g) the mixture was basified with solid sodium hydrogen carbonate, the water layer was extracted with chloroform (3x70 mL) to give the crude mixture (**2**) and (**3**) of products.

Reactions with Me_3SiN_3: To a mixture of 1 mmol of 5-oxo derivative (**1**) or (**4**) in CH_2Cl_2 (20 mL) and concentrated sulfuric acid (1 mL) Me_3SiN_3 (594 mg, 5 mmol) in CH_2Cl_2 (4 mL) was added during 30–45 min. After stirring, the addition of cold water (25 mL) and basification (as above) the mixture was extracted with 5×25 mL of CH_2Cl_2 (8×25 mL for **5a** and **5b**).

Reaction conditions and yields of products are given in Table 1. Products (**2a–c**) and (**3a–c**) were separated on a chromatotron with $CHCl_3$/MeOH (25:1) as the eluant. Products (**2d–f**) were isolated in the pure state by crystallizing mixtures (**2d–f**) and (**3d–f**) as obtained by carrying out reactions on ice/NaCl bath. Compounds (**3d–f**) have not been isolated in the pure state. The assumption that they were formed is the result of the analysis of ^{1}H NMR spectra of mixtures **2/3**.

Analytical and spectroscopic data of products:

3-Amino-6,7,8,9-tetrahydropyrano[3,2-*c*]azepine-2,5-dione (2a): mp 229–230 °C (EtOAc); ^{1}H NMR (300 MHz) δ 1.93 (m, 2H, 8-CH_2), 2.75 (m, 2H, 9-CH_2), 3.11 (m, 2H, 7-CH_2), 5.30 (s, 2H, NH_2), 6.61 (s, 1H, 4-H), 8.03 (t, *J* 5.6, 1H, 6-H); ^{13}C NMR (75.5 MHz) δ 27.83, 29.61, 39.34, 110.60, 113.38, 131.82, 152.55, 159.47, 167.99; MS (m/z, %) 194 (M^+, 100). IR (KBr) 3436, 3359, 3313 br, 1711 br, 1696, 1638 br, 1562. Anal. Calcd for $C_9H_{10}N_2O_3$: C, 55.67; H, 5.19; N, 14.43. Found: C, 55.42; H, 5.28; N, 14.36.

3-Amino-8-methyl-6,7,8,9-tetrahydropyrano[3,2-*c*]azepine-2,5-dione (2b): mp 194–195.5 °C (EtOAc); ^{1}H NMR δ 0.92 (d, *J* 6.4, 3H, Me), 2.22-2.37 (m, 2H, 9-H$_a$, 8-H), 2.68-2.86 (m, 2H, 9-H$_b$, 7-H$_a$), 3.06-3.17 (m, 1H, 7-H$_b$), 5.32 (s, 2H, NH$_2$), 6.52 (s, 1H, 4-H), 8.03 (t, *J* 5.7, 1H, 6-H); ^{13}C NMR δ 18.69, 34.99, 36.44, 45.94, 109.81, 113.60, 132.10, 151.77, 159.53, 168.74; MS (m/z, %) 208 (M$^+$, 100). IR (KBr) 3468, 3336 br, 1704, 1699, 1659, 1598, 1559. Anal. Calcd for $C_{10}H_{12}N_2O_3$: C, 57.69; H, 5.81; N, 13.45. Found: C, 57.79; H, 5.67; N, 13.31.

3-Amino-8,8-dimethyl-6,7,8,9-tetrahydropyrano[3,2-*c*]azepine-2,5-dione (2c): mp 194–196 °C (EtOAc) (lit.,[5] mp 194–196 °C).

***N*-(2,5-Dioxo-2,5,6,7,8,9-hexahydropyrano[3,2-*c*]azepin-3-yl)benzamide (2d):** 242–244 °C (EtOH); ^{1}H NMR δ 2.00 (m, 2H, 8-CH$_2$), 2.87 (m, 2H, 9-CH$_2$), 3.18 (m, 2H, 7-CH$_2$), 7.58 (m, 3H, Ph), 7.94 (m, 2H, Ph), 8.25 (t, *J* 5.7, 1H, 6-H), 8.28 (s, 1H, 4-H), 9.60 (s, 1H, NH); ^{13}C NMR δ 27.43, 30.39, 39.22, 112.46, 122.40, 127.60, 128.51, 129.32, 132.07, 133.50, 158.38, 161.05, 165.79, 166.85; MS (m/z, %) 298 (M$^+$, 43), 105 (100). IR (KBr) 3359, 3200 br, 1715, 1669, 1655, 1599, 1571, 1528. Anal. Calcd for $C_{16}H_{14}N_2O_4$: C, 64.42; H, 4.73; N, 9.39. Found: C, 64.57; H, 4.71; N, 9.24.

***N*-(8-Methyl-2,5-dioxo-2,5,6,7,8,9-hexahydropyrano[3,2-*c*]azepin-3-yl)benzamide (2e):** 245–246 °C (EtOH/DMF); ^{1}H NMR δ 0.97 (d, *J* 6.6, 3H, Me), 2.31-2.48 (m, 2H, 9-H$_a$, 8-H), 2.77-2.97 (m, 2H, 7-H$_a$, 9-H$_b$), 3.20 (m, 1H, 7-H$_b$), 7.58 (m, 3H, Ph), 7.93 (m, 2H, Ph), 8.23 (s, 1H, 4-H), 8.26 (t, *J* 5.7, 6-H), 9.58 (s, 1H, NH); ^{13}C NMR δ 18.73, 34.77, 37.15, 45.78, 112.67, 122.67, 127.58, 128.29, 128.52, 132.09, 133.50, 158.49, 160.29, 165.82, 167.63; MS (m/z, %) 312 (M$^+$, 31), 105 (100). IR (KBr) 3411, 3200 br, 3063 br, 2958, 2924, 1720, 1655 br, 1600, 1573, 1526 br. Anal. Calcd for $C_{17}H_{16}N_2O_4$: C, 65.38; H, 5.16; N, 8.97. Found: C, 65.40; H, 4.99; N, 8.99.

***N*-(8,8-Dimethyl-2,5-dioxo-2,5,6,7,8,9-hexahydropyrano[3,2-*c*]azepin-3-yl)benzamide (2f):** mp 254–256 °C (lit.,[5] mp 254–256 °C).

3-Amino-5,7,8,9-tetrahydropyrano[3,2-*b*]azepine-2,6-dione (3a): mp 197–199 °C (EtOAc); ^{1}H NMR δ 1.99 (m, 2H, 8-CH$_2$), 2.35 (m, 2H, 7-CH$_2$), 2.64 (m, 2H, 9-CH$_2$), 5.39 (s, 2H, NH$_2$), 6.18 (s, 1H, 4-H), 8.95 (s, 1H, 5-H); ^{13}C NMR δ 22.98, 29.28, 34.44, 108.20, 118.93, 132.33, 139.84, 158.88, 173.58; MS (m/z, %) 194 (M$^+$, 100). IR (KBr) 3443, 3343, 1718, 1674, 1648, 1621, 1574. HRMS Calcd for $C_9H_{10}N_2O_3$: 194.0691. Found: 194.0697.

3-Amino-8-methyl-5,7,8,9-tetrahydropyrano[3,2-*b*]azepine-2,6-dione (3b): mp 213–216 °C (EtOAc); ^{1}H NMR δ 1.01 (d, *J* 6.8, 3H, Me), 2.10 (dd, J_1 7.5, J_2 12.8, 1H, 7-H$_a$), 2.21–2.38 (m, 2H, 7-H$_b$, 9-H$_a$), 2.44 (m, 1H, 8-H), 2.73 (dd, J_1 6.4, J_2 15.5, 1H, 9-H$_b$), 5.39 (s, 2H, NH$_2$), 6.17 (s, 1H, 4-H), 8.98 (s, 1H, 5-H); ^{13}C NMR δ 21.63, 33.17, 36.12, 41.62, 107.99, 119.17, 132.51, 140.29, 158.99, 172.44; MS (m/z, %) 208 (M$^+$, 100). IR (KBr) 3468, 3359,1709, 1654, 1610, 1563. Anal. Calcd for $C_{10}H_{12}N_2O_3$: C, 57.69; H,

5.81; N, 13.45. Found: C, 57.38; H, 5.94; N, 13.26.

3-Amino-8,8-dimethyl-5,7,8,9-tetrahydropyrano[3,2-*b*]azepine-2,6-dione (3c): mp 267–269 °C (decomp, EtOAc); ^{1}H NMR δ 1.03 (s, 6H, two Me), 2.08 (s, 2H, 7-CH_2), 2.36 (s, 2H, 9-CH_2), 5.41 (s, 2H, NH_2), 6.16 (s, 1H, 4-H), 9.01 (s, 1H, 5-H); ^{13}C NMR δ 28.85, 41.52, 41.96, 47.40, 107.83, 119.63, 132.71, 141.27, 159.10, 172.10; MS (m/z, %) 222 (M^+, 100). IR (KBr) 3459, 3360, 1707, 1656, 1641, 1622, 1561. Anal. Calcd for $C_{11}H_{14}N_2O_3$: C, 59.45; H, 6.35; N, 12.60. Found: C, 59.30; H, 6.21; N, 12.50.

***N*-(2,6-Dioxo-2,5,6,7,8,9-hexahydropyrano[3,2-*b*]azepin-3-yl)benzamide (3d):** ^{1}H NMR δ 2.09 (m, 2H, 8-CH_2), 2.44 (m, 2H, 7-CH_2), 2.77 (m, 2H, 9-CH_2), 8.08 (s, 1H, 4-H), 9.20 (s, 1H, 5-H), 9.52 (s, 1H, NH). These data were obtained from ^{1}H NMR spectrum of the mixture of compounds (**2d**) and (**3d**); signals for phenyl group are covered with signals of the compound (**2d**).

***N*-(8-Methyl-2,6-dioxo-2,5,6,7,8,9-hexahydropyrano[3,2-*b*]azepin-3-yl)benzamide (3e):** ^{1}H NMR δ 1.06 (d, *J* 6.6, 3H, Me), 2.19 (dd, J_1 7.4, J_2 12.9, 1H, 7-H_a), 8.05 (s, 1H, 4-H), 9.23 (s, 1H, 5-H), 9.52 (s, 1H, NH). These data were obtained from ^{1}H NMR spectrum of the mixture of compounds (**2e**) and (**3e**); all other signals of **3e** are covered with signals of the compound (**2e**).

***N*-(8,8-Dimethyl-2,6-dioxo-2,5,6,7,8,9-hexahydropyrano[3,2-*b*]azepin-3-yl)benzamide (3f):** ^{1}H NMR δ 1.09 (s, 6H, two Me), 2.19 (s, 2H, 7-CH_2), 2.50 (s, 2H, 9-CH_2), 8.05 (s, 1H, 4-H), 9.25 (s, 1H, 5-H), 9.50 (s, 1H, NH). These data were obtained from ^{1}H NMR spectrum of the mixture of compounds (**2f**) and (**3f**); all other signals of **3f** are covered with signals of the compound (**2f**).

3-Amino-7,8-dihydro-2*H*-pyrano[3,2-*c*]pyridine-2,5(6*H*)-dione (5a): mp 270–272 °C (decomp, EtOH); ^{1}H NMR δ 2.74 (t, *J* 7.2, 2H, 8-CH_2), 3.36 (dt, J_1 2.6, J_2 7.2, 2H, 7-CH_2), 5.36 (s, 2H, NH_2), 6.63 (s, 1H, 4-H), 7.59 (deg t, 1H, 6-H); ^{13}C NMR δ 25.24, 37.50, 106.61, 109.74, 132.35, 153.53, 159.08, 163.83; MS (m/z, %) 180 (M^+, 100). IR (KBr) 3468, 3319, 1724, 1666, 1620, 1570. Anal. Calcd for $C_8H_8N_2O_3$: C, 53.33; H, 4.48; N, 15.55. Found: C, 53.51; H, 4.54; N, 15.27.

***N*-(2,5-Dioxo-5,6,7,8-tetrahydro-2*H*-pyrano[3,2-*c*]pyridin-3-yl)benzamide (5b):** mp 333–336 °C (decomp, EtOH/DMF); ^{1}H NMR δ 2.90 (t, *J* 7.1, 2H, 8-CH_2), 3.45 (dt, J_1 2.7, J_2 7.1, 2H, 7-CH_2), 7.58 (m, 3H, Ph), 7.83 (deg t, 1H, 6-H), 7.94 (m, 2H, Ph), 8.31 (s, 1H, 4-H), 9.62 (s, 1H, NH); ^{13}C NMR δ 25.85, 37.16, 108.65, 122.77, 125.63, 127.60, 128.52, 132.10, 133.45, 158.05, 162.21, 162.88, 165.80; MS (m/z, %) 284 (M^+, 43), 105 (100). IR (KBr) 3367, 3219, 1720, 1679, 1662, 1584, 1532. Calcd for $C_{15}H_{12}N_2O_4$: C, 63.38; H, 4.25; N, 9.85. Found: C, 63.34; H, 4.29; N, 9.95.

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