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Synthesis and Reaction of Some 2-Alkylene-1,3-oxazolidines

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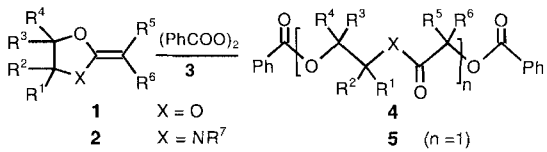
Abstract. Starting from 1,3-oxazoline **6** synthesis of ketene-O,N-acetals **2b**, **2c** is described *via* NBS bromination and HBr elimination.
The *N*-sulfonyl-oxazolidines **10**, **11** are synthesized by cyclization starting from aminoalcohol **7**, **10d** react with potassium *t*-butoxide to the oxazolidine **2d**; **11d** gives under the some conditions the ring opening product **12d**, compound **10a** is inert.

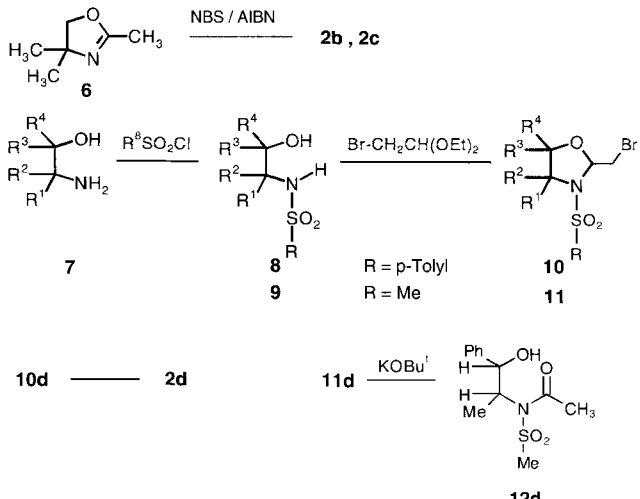
In contrast to the ketene-O,O-acetals of the type **1** which react with dibenzoyl peroxide **3** under ring opening to the polyesters of the type **4** with n > 1 [1, 2] the reaction of the ketene O,N-acetal **2a** (R=Me) with **3** leads to a simple ring opening product **5** [3, 4]. To confirm more these differences between ketene–O,O-acetals, **2b**, **2d** and **2c** were prepared and the both first mentioned compounds treated with **3** under analogous conditions. Surprisingly the reaction took not place.

The synthesis of the ketene–O,N-acetals **2b–2d** was made in different ways. Whereas the compounds **2b** and **2c** were synthesized in changing yields by reaction of the 1,3-oxazoline **6** with variable amounts of NBS in the presence of AIBN, the synthesis of **2d** (R=phenyl) was carried out with the aminoalcohol **7d**. **7d** gives the sulfonamide **8d** with *p*-toluenesulfonylchloride which reacts with bromoacetaldehyde diethyl acetal to the 1,3-oxazolidine **10d**. Potassium *t*-butoxide was used for the elimination of HBr leading to the end product **2d**.

The 1,3-oxazolidine derivatives **10a** and **11d** prepared in the same way from the aminoalcohols **7a** and **7d** show different reactions with potassium *t*-butoxide. Whereas **11d** gives the ring opening product **12d** (with trace of water), **10a** is inert under the some conditions.



2,7–12	R^1	R^2	R^3	R^4	R^5	R^6	R^7
a	Me	Me	H	H	Me	Me	Me
b	Me	Me	H	H	Br	H	Br
c	Me	Me	H	H	Br	Br	Br
d	Me	H	Ph	H	H	H	SO_2R



Scheme 1

Experimental

^1H and ^{13}C NMR were recorded on a Bruker WP 200 operating at 200 Hz (^1H) and 50 Hz (^{13}C). Chemical shifts are referred to internal standard TMS and are reported in ppm.

N-(2-Hydroxy-1-methyl-2-phenyl-ethyl)-methanesulfonamide (**9d**)

A solution of 1.51 g (13.2 mmol) of methanesulfonyl chloride (Fluka) in 5 mL CH_2Cl_2 was added dropwise to a solution of 4.05 g (26.4 mmol) of 2-amino-1-phenyl-1-propanol **7d** (Fluka)

in 10 mL CH_2Cl_2 at −10 °C. After the addition, the mixture was warmed to room temperature and stirred overnight. The precipitate was filtered and the solvent evaporated, the residue was dried and recrystallized from diethyl ether. Yield 89%, *m.p.* 101–102 °C. – ^{1}H NMR ($CDCl_3$, 250 MHz): δ/ppm = 1.08 (3H, s, CH_3), 2.90 (3H, s, CH_3SO_2), 3.76 (1H, m, -$CHCH_3$), 4.84 (1H, d, -CHOH), 7.30 (5H, aromatic H's). – ^{13}C NMR ($CDCl_3$, 62 MHz): δ/ppm = 16.11 ($\underline{C}H_3$), 41.64 ($\underline{C}H_3SO_2$), 55.13 (-$\underline{C}HCH_3$), 76.30 (-$\underline{C}$HOH), 126.30–140.28 (aromatic C's). – IR (KBr) ν/cm^{-1} = 3497, 3335, 2993, 1407, 1296, 1146, 1122, 1050, 763, 705, 518 .

$C_{10}H_{15}SNO_3$ calcd.: C 52.41 H 6.55 S 13.99 N 6.11
(229.16) found: C 52.13 H 6.54 S 14.51 N 6.05.

2-Bromomethyl-3-methanesulfonyl-4-methyl -5-phenyl-oxazolidine (**11d**)

0.50 g (2.2 mmol) compound **9d** and 0.43 g (2.2 mmol) of bromoacetaldehyde diethyl acetal (Aldrich) and catalytic amount of Amberlyst-15 (strong acid, Merck) were dissolved in 50 mL of benzene and refluxed for 30h collecting the azeotrope benzene/ethanol in a trap. Then the mixture was cooled to room temperature, filtered, the solvent evaporated, and the residue was purified by chromatography on silica gel (eluents: ethyl acetate/heptane). Yield 55 %, *m.p.* 84–85 °C. – ^{1}H NMR ($CDCl_3$, 250 MHz): δ/ppm = 0.93 (3H, d, CH_3), 3.03 (3H, s, CH_3SO_2), 3.64 (1H, dd, -CH_2Br), 3.83 (1H, dd, –CH_2Br), 4.20 (1H, m, -$CHCH_3$), 5.12 (1H, d, -CH–O), 5.32 (1H, dd, O–CH–N), 7.34 (5H,aromatic H's). – ^{13}C NMR ($CDCl_3$, 62 MHz): δ/ppm = 17.57 ($\underline{C}H_3$), 34.03 (-$\underline{C}H_2$Br), 39.12 ($\underline{C}H_3SO_2$), 58.45 (-$\underline{C}HCH_3$), 82.13 (-$\underline{C}$H–O), 88.23 (O–$\underline{C}$H–N), 126.10–134.73 (aromatic C's). – IR (KBr) ν/cm^{-1} = 2976, 1455, 1337, 1165, 1025, 998, 753, 710, 571.

$C_{12}H_{16}SBrNO_3$
(334.09) calcd.: C 43.14 H 4.79 S 9.60 Br 23.92 N 4.19
found: C 43.60 H 4.66 S 9.51 Br 23.01 N 4.35.

N-(2-Hydroxy-1-methyl-2-phenyl-ethyl)-N-acetylmethanesulfonamide (**12d**)

0.22 g (2 mmol) of potassium *t*-butoxide in 5 mL of THF (dry) were added dropwise to a solution of 0.60 g (1.8 mmol) compound **11d** in 5 mL of THF (dry) at −10 °C. Then the mixture was warmed to room temperature and refluxed for 1h. After cooling, the precipitate was filtered, the solvent evaporated, and the residue was washed with a solution of benzene/hexane 1:1 at 80 °C and hot filtrated. The solvents were evaporated, and the rest was recrystallized from hexane (dry) under argon. Yield 70%, *m.p.* 39–40 °C. – ^{1}H NMR ($CDCl_3$, 250 MHz): δ/ppm = 1.17 (3H, d, CH_3), 2.13 (3H, s, CH_3CO), 2.76 (3H, s, CH_3SO_2), 3.93 (1H, m, -$CHCH_3$), 5.69 (1H, d, -CHOH), 7.33 (5H, aromatic H's). – ^{13}C NMR ($CDCl_3$, 62 MHz): δ/ppm = 18.19 ($\underline{C}H_3$), 21.08 ($\underline{C}H_3CO$), 41.90 ($\underline{C}H_3SO_2$), 53.34 (-$\underline{C}HCH_3$), 77.56 (-$\underline{C}$HOH), 126.99–136.37 (aromatic C's), 169.91 ($\underline{C}O$).

$C_{12}H_{17}SNO_4$ calcd.: C 53.14 H 6.27 S 11.82 N 5.16
(271.18) found: C 52.94 H 6.02 S 11.95 N 5.02.

N-(2-Hydroxy-1-methyl-2-phenyl-ethyl)-4-methyl-benzenesulfonamide (**8d**)

10.16 g (53.3 mmol) *p*-toluenesulfonyl chloride in 50 mL CH_2Cl_2 were added dropwise to a solution of 10 g (53.3 mmol) of **7d** and 33.44 mL Et_3N (239.9 mmol) in 100 mL CH_2Cl_2 at −40 °C. After the addition the mixture was stirred at this temperature for 4h and then warmed to room temperature and stirred overnight. The precipitate was filtered, the solvent evaporated and the residue was dried and recrystallized from diethyl ether. Yield 89%, *m.p.* 114–115 °C. – ^{1}H NMR ($CDCl_3$, 250 MHz): δ/ppm = 0.80 (3H, s, CH_3), 2.39 (3H, s, CH_3), 3.53 (1H, m, -$CHCH_3$), 4.77 (1H, d, -CHOH), 7.18–7.30 (7H, aromatic H's), 7.75 (2H, aromatic H's). – ^{13}C NMR ($CDCl_3$, 62 MHz): δ/ppm = 14.44 ($\underline{C}H_3$), 21.45 ($\underline{C}H_3$), 54.95 (-$\underline{C}HCH_3$), 75.64 (-$\underline{C}$HOH), 126.01–143.46 (aromatic C's). – IR (Kr): ν/cm^{-1} = 3421, 3182, 2982, 1444, 1323, 1155, 1140, 1091, 1081, 973, 700, 666, 559 .

$C_{16}H_{19}SNO_3$ calcd.: C 62.97 H 6.23 S 10.51 N 4.59
(305.16) found: C 62.7 H 6.40 S 10.43 N 4.60.

2-Bromomethyl-4-methyl-5-phenyl-3-(p-toluenesulfonyl)-oxazolidine (**10d**)

17.94 g (58.8 mmol) compound **8d**, 11.59 g (58.8 mmol) of bromoacetaldehyde diethyl acetal (Aldrich) and catalytic amount of Amberlyst 15 (strong acid, Merck) were dissolved in 100 mL of benzene and refluxed for 31h collecting the azeotrope benzene/ethanol in a trap. Then the mixture was cooled to room temperature, filtered, the solvent evaporater and the residue purified by chromatography on silica gel (eluents: diethyl acetate/heptane). Yield 90%, *m.p.* 104–105 °C. – ^{1}H NMR ($CDCl_3$, 250 MHz): δ/ppm = 0.85 (3H, d, CH_3), 2.45 (3H, s, CH_3), 3.63 (1H, dd, -CH_2Br), 3.90 (1H, dd, -CH_2Br), 4.03 (1H, m, -$CHCH_3$), 4.37 (1H, d, -CH–O), 5.18 (1H, dd, O–CH–N), 7.15–7.40 (7H, aromatic H's), 7.80 (2H, aromatic H's). – ^{13}C NMR ($CDCl_3$, 62 MHz): δ/ppm = 17.60 ($\underline{C}H_3$), 21.59 ($\underline{C}H_3$), 34.60 (-$\underline{C}H_2$Br), 58.47 (-$\underline{C}HCH_3$), 81.49 (-$\underline{C}$H–O), 88.60 (O–$\underline{C}$H–N), 125.91–144.67 (aromatic C's). – IR (KBr): ν/cm^{-1} = 3246, 2978, 1433, 1327, 1167, 1151,1039, 704.

$C_{18}H_{20}SBrNO_3$
(410.15) calcd.: C 52.71 H 4.88 S 7.82 Br 19.48 N 3.41
found: C 52.54 H 5.10 S 7.70 Br 19.13 N 3.55.

4-Methyl-2-methylene-5-phenyl-3-(p-toluenesulfonyl)-oxazolidine (**2d**)

5.00 g (12 mmol) of compound **10d** in 10 mL THF (dry) were added dropwise into a solution of 1.64 g (15 mmol) potassium *t*-butoxide in 5 mL of THF (dry) at −10°C. After the addition the mixture was warmed to room temperature and then stirred 1h at 50 °C. The precipitate was filtered, the solvent evaporated, and the residue was washed with a solution of benzene/hexane 1:1 and hot filtrated. The solvents were evaporated and the rest was recrystallized from hexane. Yield 86%, *m.p.* 64–65 °C. – H NMR (DMSO-d_6, 250 MHz): δ/ppm = 0.81 (3H, d, CH_3), 2.41 (3H, s, CH_3), 3.90 (1H, d, CH_2=C-), 4.13 (1H, d, CH_2=C-), 4.81 (1H, -CH-), 4.86 (1H, -CH-), 7.31 (5H, aromatic H's), 7.47 (2H, aromatic H's), 7.90 (2H, aromatic H's). – ^{13}C NMR (DMSO-d_6, 62 MHz): δ/ppm = 16.68 ($\underline{C}H_3$CH-), 21.03 ($\underline{C}H_3$), 58.31 (-$\underline{C}HCH_3$), 68.39 ($\underline{C}H_2$=C-), 80.06 (-$\underline{C}$H–O), 125.86–144.73 (aromatic C's), 151.02 (-$\underline{C}$=CH_2). – IR (KBr): ν/cm^{-1} = 2928, 1673, 1350, 1168, 1094, 1002, 661, 593.

$C_{18}H_{19}SNO_3$ calcd.: C 65.65 H 5.77 S 9.74 N 4.25
(329.24) found: C 65.58 H 5.32 S 8.35 N 3.57.

N-(Hydroxy-1,1-dimethyl-ethyl)-4-methyl-benzenesulfonamide (**8a**)

19.90 mL (142.8 mmol) Et_3N was added dropwise to a solution of 6.36 g (71.4 mmol) **7a** and 13.61 g (71.4 mmol) of *p*-toluenesulfonyl chloride in 50 mL CH_2Cl_2. After the addition the mixture was stirred 24 h and then washed with solution of 1M H_2SO_4, the organic phase was dried with sodium sulfate, and the solvent evaporated. The residue was dried and recrystallized from hexane. Yield 50%, *m.p.* 92–93 °C. – ^{1}H NMR ($CDCl_3$, 250 MHz): δ/ppm = 1.07 (6H, s, $2CH_3$), 2.37 (3H, s, CH_3), 3.40 (2H, s, $-CH_2OH$), 7.24 (2H, aromatic H's), 7.77 (2H, aromatic H's). – ^{13}C NMR ($CDCl_3$, 62 MHz): δ/ppm = 21.40 ($\underline{C}H_3$), 24.31 ($2\underline{C}H_3$), 57.77 ($-\underline{C}(CH_3)_2$), 70.10 ($-\underline{C}H_2OH$), 126.89–143.10 (aromatic C's). – IR(KBr): ν/cm^{-1} = 3296, 3265, 2930, 1311, 1137, 1094, 660.
$C_{11}H_{17}SNO_3$ calcd.: C 54.33 H 6.99 S 13.18 N 5.76
(243.17) found: C 54.28 H 6.68 S 13.38 N 5.88.

2-Bromomethyl-4,4-dimethyl-3-(p-toluenesulfonyl)-oxazolidine (**10a**)

8.29 g (34.1 mmol) compound **8a**, 6.72 g (34.1 mmol) bromoacetaldehyde diethyl acetal (Aldrich) and 0.10 g of Amberlyst-15 (strong acid, Merck) were dissolved in 25 mL of benzene and refluxed for 24 h collecting the azeotrope benzene/ethanol in a trap. After cooling to room temperature the mixture was filtered, the solvent was evaporated, and the residue was purified by chromatography on silica gel (eluents: diethyl acetate/heptane), yield 65%, *m.p.* 61–62 °C. – ^{1}H NMR ($CDCl_3$, 250 MHz): δ/ppm = 1.27 (3H, s, CH_3), 1.43 (3H, s, CH_3), 2.37 (3H, s, CH_3), 3.45 (1H, dd, $-CH_2Br$), 3.63 (1H, d, $-CH_2-O-$), 3.72 (1H, dd, $-CH_2Br$), 3.82 (1H, d, $-CH_2-O-$), 5.33 (1H, dd, O–CH–N), 7.26 (2H, aromatic H's), 7.72 (2H, aromatic H's). – ^{13}C NMR ($CDCl_3$, 62 MHz): δ/ppm = 21.36 ($\underline{C}H_3-$), 24.24 ($\underline{C}H_3$), 26.68 ($\underline{C}H_3$), 33.53 ($-\underline{C}H_2-Br$), 64.07 ($-\underline{C}(CH_3)_2$), 78.44 ($-\underline{C}H_2-O$), 90.60 (O–$\underline{C}$H–N), 127.48–143.84 (aromatic C's). – IR (KBr): ν/cm^{-1} =2934, 2872, 1716, 1500, 1451, 1317, 1189, 1031.
$C_{13}H_{18}SBrNO_3$
(348.10) calcd.: C 44.85 H 5.17 S 9.21 Br 22.96 N 4.02
found: C 45.59 H 5.43 S 9.78 Br 21.95 N 4.15.

3-Bromo-2-bromomethylene-4,4-dimethyl-oxazolidine (**2b**) *and 3-Bromo-2-dibromo- methylene-4,4-dimethyl-oxazolidine* (**2c**)

0.50 g (4.4 mmol) 2,4,4-trimethyl-4,5-dihydrooxazol (Merck) compound **6**, 0.786 g (4.4 mmol) NBS (*N*-bromosuccinimide, Merck) and a catalytic amount of AIBN (2,2'-azoisobutyronitrile) were dissolved in 50 mL of CCl_4 and refluxed until the end of reaction (1 h). After cooling to room temperature, the precipitate was filtered , the solvent evaporated, and the residue was purified by chromatography on silica gel (eluents: diethyl acetate/heptane). Yield 20% of **2b**, *m.p.* 111–112 °C, yield 40% of **2c**, *m.p.* 117–118 °C. With 3 eq. of NBS, only **2c** was obtained with the yield of 77%. – ^{1}H NMR ($CDCl_3$, 250 MHz): δ/ppm = 1.30 (6H, s, $2CH_3$), 4.13 (2H, s, $-CH_2-O$), 6.05 (1H, s, -CH=C-). – ^{13}C NMR ($CDCl_3$, 62 MHz): δ/ppm = 27.50 ($2\underline{C}H_3$), 27.71 (-C=$\underline{C}$HBr), 68.20 ($-\underline{C}(CH_3)_2$), 80.73 ($-\underline{C}H_2-O$), 160.80 (O–$\underline{C}$–N). – IR (KBr): ν/cm^{-1} = 2972, 1658, 1306, 981, 617.
2b: $C_6H_9Br_2NO$ calcd.: C 26.60 H 3.32 Br 59.00 N 5.17
(270.88) found: C 26.01 H 3.10 Br 57.13 N 5.02.
^{1}H NMR ($CDCl_3$, 250 MHz): δ/ppm = 1.37 (6H, s, $2CH_3$), 4.31 (2H, s, $-CH_2-O$). – ^{13}C NMR ($CDCl_3$, 62 MHz): δ/ppm = 20.68 ($-\underline{C}(Br)_2$), 27.13 ($2\underline{C}H_3$), 68.79 ($-\underline{C}(CH_3)_2$), 82.39 ($-\underline{C}H_2-O$), 161.18 (O–$\underline{C}$–N). – IR (KBr): ν/cm^{-1} = 2959, 1649, 1279, 990, 722, 618.
2c: $C_6H_8Br_3NO$ calcd.: C 20.60 H 2.29 Br 68.53 N 4.00
(349.79) found: C 20.64 H 2.52 Br 65.27 N 4.10.

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