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# General Procedure for the Synthesis of Spirocyclic 3-Hydroxy- and 3-Oxotetrahydrofurans Containing Carbo- and Heterocyclic Fragments

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**Abstract**—Reactions of cyclopentanone, cyclohexanone, N-substituted pyrrolidin-3-one and piperidin-4-one, and tetrahydropyran-4-one with allyl bromide in the presence of zinc and ammonium chloride gave the corresponding geminal hydroxy allyl derivatives. Treatment of the latter with sodium periodate in the presence of sodium metabisulfite resulted in their oxidative cyclization with formation of oxa spirocyclic alcohols containing carbo- and heterocyclic fragments. Swern oxidation of the spiro alcohols afforded the corresponding ketones which were characterized as 2,4-dinitrophenylhydrazones.

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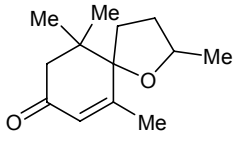
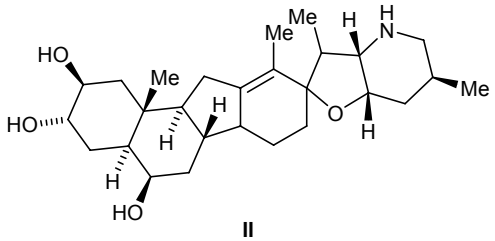
Spirocyclic derivatives of tetrahydrofuran attract interest as potential biologically active substances. For example, compounds **I** and **II** were isolated from plants [1, 2], in particular from tea [3]. 8-Methyl-1-oxa-8-azaspiro[4.5]decan-3-one, 2,8-dimethyl-1-oxa-8-azaspiro[4.5]decan-3-one and their derivatives were reported to act as muscarinic cholinomimetics [4], i.e., their activity is analogous to that of such medical agents as Aceclidine and Pilocarpine.




**I**

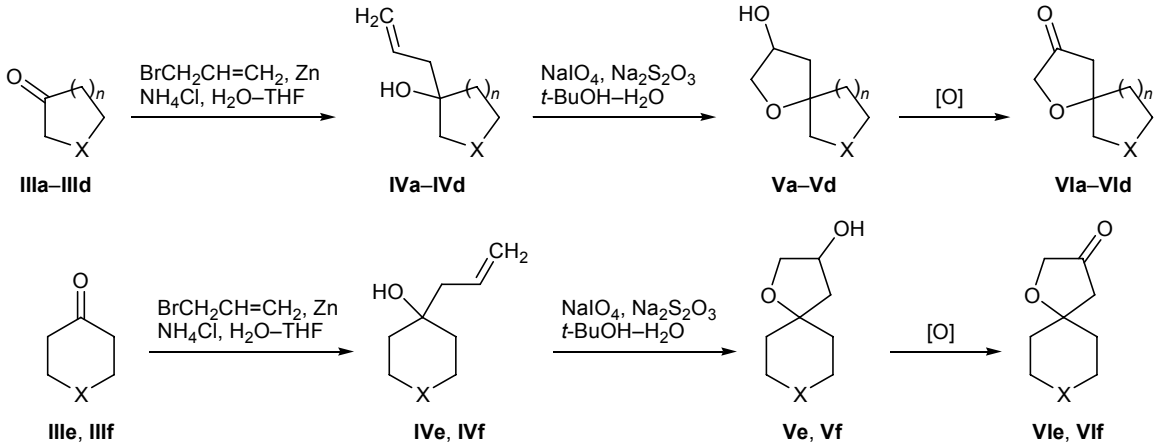



**II**

Known methods for the synthesis of oxaspirononane and oxaspirodecane systems [4–11] are quite specific and tedious, whereas the overall yields of target products **VIa** and **VIb** do not exceed 20%. Moreover, in some cases highly toxic reagents, in particular mercury(II) salts [5], lead(IV) acetate [8], and selenium(II) compounds [9], or expensive rhodium catalysts [11] were used, which may also be regarded as disadvantages.

Taking into account the above stated and the results of our previous studies [12] on new heterocyclic spiro compounds, the goal of the present work was to develop a general procedure for the synthesis of spirocyclic 3-hydroxy- and 3-oxotetrahydrofuran derivatives containing carbo- and heterocyclic fragments. Interest in such compounds is determined by broad potential of their application in preparative organic synthesis due to the presence of functional groups. As starting compounds we used accessible carbo- and heterocyclic ketones, cyclopentanone (**IIIa**), cyclohexanone (**IIIb**), *tert*-butyl 3-oxopyrrolidine-1-carboxylate (**IIIc**), *tert*-butyl 3-oxopiperidine-1-carboxylate (**IIId**), *tert*-butyl-4-oxopiperidine-1-carboxylate (**IIIe**), and tetrahydropyran-4-one (**IIIf**). Ketones **IIIa**–**IIIf** fairly readily reacted with allyl bromide in the presence of zinc dust in tetrahydrofuran–saturated aqueous ammonium chloride over a period of 10–12 h at room temperature under vigorous stirring (TLC monitoring). As a result, the corresponding geminal allyl hydroxy derivatives **IVa**–**IVf** were formed in almost quantitative yield (Scheme 1); their structure was confirmed by elemental analyses, and IR, $^1$H NMR, and mass spectra.

**Scheme 1.**




X = $CH_2$ (**a**, **b**), *t*-BuOCON (**c**, **d**, **e**), O (**f**); *n* = 1 (**a**, **c**), 2 (**b**, **d**).

The IR spectra of **IVa**–**IVf** contained absorption bands in the regions 3500–3480 and 1605–1617 $cm^{-1}$ due to stretching vibrations of the O–H and C=C bonds, respectively. In the $^1H$ NMR spectra of **IVa**–**IVf**, multiplet signals typical of allyl group were observed at δ 2.15–2.30 (2H, $CH_2$), 5.05–5.20 (2H, CH=C**H**$_2$), and 5.85–5.95 ppm (1H, C**H**=$CH_2$).

The key step in the synthesis of oxaspirocyclic systems from alcohols **IVa**–**IVf** may be oxidative cyclization which is generally [13] characterized by low selectivity and poor yield. The results of our experiments showed that the optimal and most general conditions for oxidative cyclization of compounds **IVa**–**IVf** include treatment with sodium periodate in the presence of sodium metabisulfite in aqueous *tert*-butyl alcohol at 50°C (10–12 h) and subsequent stirring for 10 h at room temperature. After chromatographic purification, the yields of spirocyclic alcohols **Va**–**Vf** were 45–50%, and the *tert*-butoxycarbonyl (Boc) protecting group remained unchanged.

Compounds **Va**–**Vf** displayed in the IR spectra absorption bands in the region 3478–3445 $cm^{-1}$ due to stretching vibrations of the hydroxy group. The IR spectra of **Vc**–**Ve** also contained absorption bands at 1695–1690 $cm^{-1}$, which belong to stretching vibrations of the ester carbonyl group. The OH proton resonated in the $^1H$ NMR spectra of **Va**–**Vf** at δ 4.42–4.83 ppm, the C**H**OH proton gave a multiplet at δ 3.78–4.04 ppm, and the doublet at δ 3.28–3.57 ppm was assigned to protons in the methylene group neighboring to the endocyclic oxygen atom.

The structure of alcohols **Va**–**Vf** was also confirmed by their oxidation into the corresponding ketones **VIa**–**VIf** (Scheme 1). Here, the most effective was oxidation according to Swern [14], which ensured 82–97% yield of compounds **VIa**–**VIf**. Other oxidants, e.g., pyridinium chlorochromate [15] (yield of **VIa** and **VIb** 45–52%), turned out to be less effective. The IR spectra of **VIa**–**VIf** contained a new strong absorption band in the region 1760–1728 $cm^{-1}$ due to stretching vibrations of the ketone carbonyl group. In the $^1H$ NMR spectra of **VIa**–**VIf** singlets at δ 2.32–2.44 ($CH_2C$=O) and 3.96–3.98 ppm ($OCH_2C$=O) were observed. The presence of a carbonyl group in compounds **VIa**–**VIf** was confirmed by the reaction with 2,4-dinitrophenylhydrazine which quantitatively afforded the corresponding crystalline 2,4-dinitrophenylhydrazones **VIIa**–**VIIf** with sharp melting points.

## EXPERIMENTAL

The IR spectra were recorded in KBr on a Specord 75IR spectrometer. The $^1H$ NMR spectra were measured on a Bruker DPX-400 instrument at 400 MHz from solutions in $CDCl_3$ using hexamethyldisiloxane as internal reference. The mass spectra (atmospheric pressure chemical ionization) were obtained on a Thermo Finnigan Surveyor MSQ GC–MS system (USA). The progress of reactions was monitored by TLC on Silufol UV-254 plates using hexane–ethyl acetate (1 : 1 by volume) as eluent. Silicagel 60 (Merck) was used for column chromatography.

**1-Allylcyclopentan-1-ol (IVa).** Zinc dust, 13 g (0.2 mol), was slowly added under vigorous stirring to a mixture of 8.4 g (0.1 mol) of cyclopentanone (**IIIa**), 30.25 g (0.25 mol) of allyl bromide, 30 ml of THF, and 100 ml of a saturated aqueous solution of ammonium chloride in such a way that the temperature did not exceed 40°C. The mixture was then stirred for 10 h at

room temperature, 100 ml of 10% aqueous sulfuric acid was added, the mixture was filtered, the organic phase was separated, and the aqueous phase was saturated with sodium chloride and extracted with diethyl ether. The extracts were combined with the organic phase and dried over anhydrous sodium sulfate, and the solvent was distilled off under reduced pressure. Yield 11.4 g (90%), light yellow liquid. IR spectrum, ν, $cm^{-1}$: 3500 (OH), 1617 (C=C). $^1H$ NMR spectrum, δ, ppm: 1.58–1.65 m (4H, $CH_2$), 1.81–1.87 m (4H, $CH_2$), 2.15 d (2H, 1-$CH_2$), 3.16 s (1H, OH), 5.05 m (2H, CH=C**H**$_2$), 5.85 m (1H, C**H**=$CH_2$). Mass spectrum: *m*/*z* 127 $[M + H]^+$. Found, %: C 76.28; H 11.18. $C_8H_{14}O$. Calculated, %: C 76.19; H 11.11. *M* 126.

Compounds **IVb** and **IVf** were synthesized in a similar way.

**1-Allylcyclohexan-1-ol (IVb).** Yield 96%, light yellow liquid. IR spectrum, ν, $cm^{-1}$: 3496 (OH), 1612 (C=C). $^1H$ NMR spectrum, δ, ppm: 1.43–1.54 m (6H, $CH_2$), 1.68–1.79 m (4H, $CH_2$), 2.21 d (2H, 1-$CH_2$), 3.24 s (1H, OH), 5.06 m (2H, CH=C**H**$_2$), 5.87 m (1H, C**H**=$CH_2$). Mass spectrum: *m*/*z* $[M + 1]^+$ 141. Found, %: C 77.38; H 11.26. $C_9H_{16}O$. Calculated, %: C 77.14; H 11.43. *M* 140.

**4-Allyltetrahydropyran-4-ol (IVf).** Yield 98%, colorless liquid. IR spectrum, ν, $cm^{-1}$: 3496 (OH), 1615 (C=C). $^1H$ NMR spectrum, δ, ppm: 1.42–1.53 m (3H, $CH_2$, OH), 1.73 m (2H, $CH_2$), 2.25 d (2H, 4-$CH_2$), 3.80 m (4H, $CH_2OCH_2$), 5.19 m (2H, CH=C**H**$_2$), 5.88 m (1H, C**H**=$CH_2$). Mass spectrum: *m*/*z* 143 $[M + H]^+$. Found, %: C 67.43; H 9.75. $C_8H_{14}O_2$. Calculated, %: C 67.61; H 9.86. *M* 142.

***tert*-Butyl 3-allyl-3-hydroxypyrrolidine-1-carboxylate (IVc).** Zinc dust, 13 g (0.2 mol), was slowly added under vigorous stirring to a mixture of 18.5 g (0.1 mol) of *tert*-butyl 3-oxopyrrolidine-1-carboxylate (**IIIc**), 30.25 g (0.25 mol) of allyl bromide, 50 ml of THF, and 100 ml of a saturated aqueous solution of ammonium chloride in such a way that the temperature did not exceed 40°C. The mixture was stirred for 12 h at room temperature (TLC monitoring), 100 ml of 10% aqueous sulfuric acid was added, the mixture was filtered, the organic phase was separated, and the aqueous phase was extracted with ethyl acetate. The extracts were combined with the organic phase and dried over anhydrous sodium sulfate, and the solvent was distilled off under reduced pressure. Yield 22.5 g (99%), light yellow oily liquid. IR spectrum, ν, $cm^{-1}$: 3486 (OH), 1689 (C=O), 1605 (C=C). $^1H$ NMR spectrum, δ, ppm: 1.43 s (9H, *t*-Bu), 1.88 m (2H, $CH_2$), 2.25 d (2H, 3-$CH_2$), 3.28 s (1H, OH), 3.51 d (4H, $CH_2NCH_2$), 5.18 m (2H, CH=C**H**$_2$), 5.93 m (1H, C**H**=$CH_2$). Mass spectrum, *m*/*z*: 228 $[M + H]^+$, 171 $[M - 57 + H]^+$, 127 $[M - 101 + H]^+$. Found, %: C 63.61; H 9.43; N 6.02. $C_{12}H_{21}NO_3$. Calculated, %: C 63.44; H 9.25; N 6.17. *M* 227.

Compounds **IVd** and **IVe** were synthesized in a similar way.

***tert*-Butyl 3-allyl-3-hydroxypiperidine-1-carboxylate (IVd).** Yield 98%, light yellow oily liquid. IR spectrum, ν, $cm^{-1}$: 3480 (OH), 1690 (C=O), 1608 (C=C). $^1H$ NMR spectrum, δ, ppm: 1.48 s (9H, *t*-Bu), 1.54–1.78 m (4H, $CH_2$), 2.27 m (3H, 3-$CH_2$, OH), 3.03 d and 3.68 m (2H each, $NCH_2$), 5.18 m (2H, CH=C**H**$_2$), 5.91 m (1H, C**H**=$CH_2$). Mass spectrum, *m*/*z*: 242 $[M + H]^+$, 185 $[M - 57 + H]^+$, 141 $[M - 101 + H]^+$. Found, %: C 64.45; H 9.28; N 5.63. $C_{13}H_{23}NO_3$. Calculated, %: C 64.73; H 9.54; N 5.81. *M* 241.

***tert*-Butyl 4-allyl-4-hydroxypiperidine-1-carboxylate (IVe).** Yield 100%, colorless oily liquid. IR spectrum, ν, $cm^{-1}$: 3486 (OH), 1692 (C=O), 1610 (C=C). $^1H$ NMR spectrum, δ, ppm: 1.39 s (9H, *t*-Bu), 1.45–1.62 m (4H, $CH_2$), 2.16 d (2H, 4-$CH_2$), 2.28 s (1H, OH), 3.04 m and 3.64 m (2H each, $NCH_2$), 5.08 m (2H, CH=C**H**$_2$), 5.88 m (1H, C**H**=$CH_2$). Mass spectrum, *m*/*z*: 242 $[M + H]^+$, 185 $[M - 57 + H]^+$, 141 $[M - 101 + H]^+$. Found, %: C 64.68; H 9.41; N 5.56. $C_{13}H_{23}NO_3$. Calculated, %: C 64.73; H 9.54; N 5.81. *M* 241.

**1-Oxaspiro[4.4]nonan-3-ol (Va).** A solution of 19 g (0.1 mol) of $Na_2S_2O_5$ in 80 ml of water was added dropwise over a period of 2 h to a mixture of 12.6 g (0.1 mol) of compound **IVa**, 21.4 g (0.1 mol) of $NaIO_4$, 150 ml of *tert*-butyl alcohol, and 50 ml of water under stirring at 50°C. The mixture was stirred for 10 h at 50°C and for 10 h at room temperature, the dark brown organic layer was separated, and the aqueous phase was saturated with sodium chloride and extracted with ethyl acetate. The extracts were combined with the organic phase and washed with a saturated aqueous solution of sodium thiosulfate, the resulting colorless solution was dried over anhydrous sodium sulfate, the solvent was removed under reduced pressure, and the oily residue was purified by column chromatography on silica gel using ethyl acetate–hexane (2 : 1) as eluent. Yield 6.8 g (48%), colorless oily liquid. IR spectrum: ν 3478 $cm^{-1}$ (OH). $^1H$ NMR spectrum, δ, ppm: 1.51–1.63 m (4H, $CH_2$), 1.75–1.84 m (4H, $CH_2$), 1.92 d (2H, $CH_2$), 3.28 d (2H, $OCH_2$), 3.87 m (1H, CHO), 4.45 s (1H, OH). Found, %: C 67.52; H 9.73. $C_8H_{14}O_2$. Calculated, %: C 67.61; H 9.86.

Compounds **Vb** and **Vf** were synthesized in a similar way.

**1-Oxaspiro[4.5]decan-3-ol (Vb).** Yield 50%, colorless oily liquid. IR spectrum, ν, $cm^{-1}$: 3464 (OH). $^1H$ NMR spectrum, δ, ppm: 1.41–1.52 m (6H, $CH_2$), 1.61–1.73 m (4H, $CH_2$), 2.01 d (2H, $CH_2$), 3.34 d (2H, $OCH_2$), 3.83 m (1H, CHO), 4.42 s (1H, OH). Found, %: C 69.13; H 10.73. $C_9H_{16}O_2$. Calculated, %: C 69.23; H 10.26.

**1,8-Dioxaspiro[4.5]decan-3-ol (Vf).** Yield 46%, colorless oily liquid. IR spectrum: ν 3475 $cm^{-1}$ (OH). $^1H$ NMR spectrum, δ, ppm: 1.18–2.08 m (6H, $CH_2$), 3.37 s (1H, OH), 3.62–4.50 m (7H, $CH_2O$, CHO). Found, %: C 60.58; H 8.73. $C_8H_{14}O_3$. Calculated, %: C 60.76; H 8.86.

***tert*-Butyl 3-hydroxy-1-oxa-7-azaspiro[4.4]-nonane-7-carboxylate (Vc).** A solution of 19 g (0.1 mol) of $Na_2S_2O_5$ in 80 ml of water was added over a period of 1 h to a mixture of 22.7 g (0.1 mol) of compound **IVc**, 21.4 g (0.1 mol) of $NaIO_4$, 150 ml of *tert*-butyl alcohol, and 50 ml of water under stirring at 50°C. The mixture was stirred for 12 h at 50°C and for 10 h at room temperature, the dark brown organic layer was separated, and the aqueous layer was extracted with ethyl acetate. The extracts were combined with the organic phase and washed with a saturated aqueous solution of sodium thiosulfate, the resulting colorless solution was dried over anhydrous sodium sulfate, the solvent was distilled off under reduced pressure, and the oily residue was purified by column chromatography on silica gel using acetone as eluent. Yield 10.9 g (45%), thick yellow–brown oily liquid. IR spectrum, ν, $cm^{-1}$: 3445 (OH), 1690 (C=O). $^1H$ NMR spectrum, δ, ppm: 1.42 s (9H, *t*-Bu), 1.86 m (2H, $CH_2$), 2.02 d (2H, $CH_2$), 3.31 s and 3.52 s (2H each, $NCH_2$), 3.57 d (2H, $CH_2O$), 4.02 m (1H, CHO), 4.83 s (1H, OH). Mass spectrum, *m*/*z*: 244 $[M + H]^+$, 187 $[M - 57 + H]^+$, 143 $[M - 101 + H]^+$. Found, %: C 59.48; H 8.54; N 5.63. $C_{12}H_{21}NO_4$. Calculated, %: C 59.26; H 8.64; N 5.76. *M* 243.

Compounds **Vd** and **Ve** were synthesized in a similar way.

***tert*-Butyl 3-hydroxy-1-oxa-7-azaspiro[4.5]-decane-7-carboxylate (Vd).** Yield 47%, thick light brown oily liquid. IR spectrum, ν, $cm^{-1}$: 3478 (OH), 1692 (C=O). $^1H$ NMR spectrum, δ, ppm: 1.44 s (9H, *t*-Bu), 1.63–1.80 m (4H, $CH_2$), 2.01 d (2H, $CH_2$), 3.15–3.45 m (4H, $NCH_2$, $CH_2O$), 3.80–4.01 m (3H, $NCH_2$, CHO), 4.50 s (1H, OH). Mass spectrum, *m*/*z*: 258 $[M + H]^+$, 201 $[M - 57 + H]^+$, 158 $[M - 101 + H]^+$. Found, %: C 60.42; H 8.76; N 5.28. $C_{13}H_{23}NO_4$. Calculated, %: C 60.70; H 8.95; N 5.45. *M* 257.

***tert*-Butyl 3-hydroxy-1-oxa-8-azaspiro[4.5]-decane-8-carboxylate (Ve).** Yield 48%, thick yellow–brown oily liquid. IR spectrum, ν, $cm^{-1}$: 3486 (OH), 1692 (C=O). $^1H$ NMR spectrum, δ, ppm: 1.39 s (9H, *t*-Bu), 1.42–1.84 m (6H, $CH_2$), 322–3.40 m (4H, $NCH_2$, $CH_2O$), 3.56–3.79 m (2H, $NCH_2$), 4.30 m (1H, CHO), 4.73 s (1H, OH). Mass spectrum, *m*/*z*: 258 $[M + H]^+$, 201 $[M - 57 + H]^+$, 158 $[M - 101 + H]^+$. Found, %: C 60.43; H 8.54; N 5.41. $C_{13}H_{23}NO_4$. Calculated, %: C 60.70; H 8.95; N 5.45. *M* 257.

**1-Oxaspiro[4.4]nonan-3-one (VIa).** *a*. Dimethyl sulfoxide, 58.5 g (0.75 mol), was added at –70°C to a solution of 47.6 g (0.375 mol) of oxalyl chloride in 300 ml of anhydrous methylene chloride, the mixture was stirred for 0.5 h, and a solution of 42.6 g (0.3 mol) of compound **Va** in 200 ml of anhydrous methylene chloride was added at –70°C. The mixture was stirred for 1 h, 80.8 g (0.8 mol) of triethylamine in 300 ml of methylene chloride was added, and the mixture was stirred for 0.5 h at –70°C and for 10 h at room temperature. The dark organic solution was washed with two portions of 20% aqueous citric acid, dried over anhydrous sodium sulfate, and evaporated, and the residue was distilled under reduced pressure. Yield 36.1 g (86%), bp 68–70°C (1 mm). IR spectrum: ν 1756 $cm^{-1}$ (C=O). $^1H$ NMR spectrum, δ, ppm: 1.48–1.62 m (4H, $CH_2$), 1.73–1.85 m (4H, $CH_2$), 2.32 s (2H, $CH_2C$=O), 3.96 s (2H, $OCH_2$). Found, %: C 68.42; H 8.24. $C_8H_{12}O_2$. Calculated, %: C 68.57; H 8.57.

*b*. Pyridinium chlorochromate, 21.6 g (0.1 mol), was added to a solution of 14.2 g (0.1 mol) of compound **Va** in 150 ml of anhydrous methylene chloride, the mixture was stirred for 20 h at room temperature and filtered through a 3-cm layer of Celite, the sorbent was washed with 150 ml of methylene chloride, the solution was evaporated, and the residue was distilled under reduced pressure. Yield 6.3 g (45%).

Compounds **VIb** and **VIf** were synthesized in a similar way.

**1-Oxaspiro[4.5]decan-3-one (VIb).** Yield 87%, bp 79–82°C (1 mm). IR spectrum: ν 1760 $cm^{-1}$ (C=O). $^1H$ NMR spectrum, δ, ppm: 1.36–1.70 m (10H, $CH_2$), 2.30 s (2H, $CH_2C$=O), 3.98 s (2H, $OCH_2$). Found, %: C 69.95; H 9.18. $C_9H_{14}O_2$. Calculated, %: C 70.13; H 9.09.

**1,8-Dioxaspiro[4.5]decan-3-one (VIf).** Yield 83%, bp 84–86°C (1 mm), colorless oily liquid. IR spec-

trum: ν 1758 $cm^{-1}$ (C=O). $^1H$ NMR spectrum, δ, ppm: 1.16–1.79 m (4H, $CH_2$), 2.59 s (2H, $CH_2C$=O), 3.61–3.78 m (4H, $CH_2O$), 3.92 s (2H, $OCH_2C$=O). Found, %: C 61.38; H 7.45. $C_8H_{12}O_3$. Calculated, %: C 61.54; H 7.69.

***tert*-Butyl 3-oxo-1-oxa-7-azaspiro[4.4]nonane-7-carboxylate (VIc).** Dimethyl sulfoxide, 21.8 g (0.28 mol), was added at –70°C to a solution of 17.9 g (0.14 mol) of oxalyl chloride in 100 ml of anhydrous methylene chloride, the mixture was stirred for 0.5 h, a solution of 24.3 g (0.1 mol) of compound **Vc** in 80 ml of anhydrous methylene chloride was added at –70°C, the mixture was stirred for 1 h, 31.4 g (0.31 mol) of triethylamine in 100 ml of methylene chloride was added, and the mixture was stirred for 0.5 h at –70°C and for 15 h at room temperature. The dark organic solution was washed with two portions of 20% aqueous citric acid and dried over anhydrous sodium sulfate, and the solvent was distilled off under reduced pressure. Yield 23.4 g (97%), mp 71–72°C (from hexane). IR spectrum, ν, $cm^{-1}$: 1730, 1691 (C=O). $^1H$ NMR spectrum, δ, ppm: 1.42 s (9H, *t*-Bu), 1.92–2.13 m (2H, $CH_2$), 2.50 s (2H, $CH_2C$=O), 3.31 m and 3.51 m (2H each, $NCH_2$), 3.98 s (2H, $OCH_2$). Mass spectrum: *m*/*z* 142 $[M - 101 + H]^+$. Found, %: C 59.68; H 7.63; N 5.66. $C_{12}H_{19}NO_4$. Calculated, %: C 59.75; H 7.88; N 5.81. *M* 241.

Compounds **VId** and **VIe** were synthesized in a similar way.

***tert*-Butyl 3-oxo-1-oxa-7-azaspiro[4.5]decane-7-carboxylate (VId).** Yield 96%, thick yellow–brown oily liquid. IR spectrum, ν, $cm^{-1}$: 1735, 1691 (C=O). $^1H$ NMR spectrum, δ, ppm: 1.41 s (9H, *t*-Bu), 1.80 m (4H, $CH_2$), 2.30 m (2H, $CH_2C$=O), 3.35 m (4H, $NCH_2$), 4.01 s (2H, $OCH_2$). Mass spectrum: *m*/*z* 156 $[M - 101 + H]^+$. Found, %: C 60.87; H 8.31; N 5.24. $C_{13}H_{21}NO_4$. Calculated, %: C 61.18; H 8.24; N 5.49. *M* 255.

***tert*-Butyl 3-oxo-1-oxa-8-azaspiro[4.5]decane-8-carboxylate (VIe).** Yield 97%, mp 65–66°C (from hexane). IR spectrum, ν, $cm^{-1}$: 1738, 1692 (C=O). $^1H$ NMR spectrum, δ, ppm: 1.40 s (9H, *t*-Bu), 1.54–1.73 m (4H, $CH_2$), 2.42 s (2H, $CH_2C$=O), 3.31 m and 3.45 m (2H each, $NCH_2$), 3.99 s (2H, $OCH_2$). Mass spectrum: *m*/*z* 156 $[M - 101 + H]^+$. Found, %: C 61.09; H 8.17; N 5.28. $C_{13}H_{21}NO_4$. Calculated, %: C 61.18; H 8.24; N 5.49. *M* 255.

**2,4-Dinitrophenylhydrazones VIIa–VIIf (*general procedure*).** A mixture of equimolar amounts (2 mmol) of ketone **VIa**–**VIf** and 2,4-dinitrophenylhydrazine, 0.1 ml of concentrated hydrochloric acid, and 12 ml of ethanol was heated for 1 h under reflux. The mixture was cooled, diluted with 60 ml of water, and left to stand for 12 h in a refrigerator at 5–6°C. The precipitate was filtered off and recrystallized from ethanol.

Compound **VIIa**. Yield 97%, mp 118–120°C. IR spectrum, ν, $cm^{-1}$: 3385 (NH); 1628 (C=N); 1531, 1350 ($NO_2$). Found, %: C 52.31; H 4.87; N 17.64. $C_{14}H_{16}N_4O_5$. Calculated, %: C 52.50; H 5.00; N 17.50.

Compound **VIIb**. Yield 98%, mp 132–134°C. IR spectrum, ν, $cm^{-1}$: 3387 (NH); 1625 (C=N); 1532, 1348 ($NO_2$). Found, %: C 53.71; H 5.27; N 16.84. $C_{15}H_{18}N_4O_5$. Calculated, %: C 53.89; H 5.39; N 16.77.

Compound **VIIc**. Yield 96%, mp 136–137°C. IR spectrum, ν, $cm^{-1}$: 3405 (NH); 1691 (C=O); 1620 (C=N); 1531, 1352 ($NO_2$). Found, %: C 51.16; H 5.32; N 16.48. $C_{18}H_{23}N_5O_7$. Calculated, %: C 51.31; H 5.46; N 16.63.

Compound **VIId**. Yield 97%, mp 139–140°C. IR spectrum, ν, $cm^{-1}$: 3402 (NH); 1690 (C=O); 1622 (C=N); 1534, 1349 ($NO_2$). Found, %: C 52.36; H 5.64; N 15.97. $C_{19}H_{25}N_5O_7$. Calculated, %: C 52.41; H 5.75; N 16.09.

Compound **VIIe**. Yield 98%, mp 148–149°C. IR spectrum, ν, $cm^{-1}$: 3402 (NH); 1692 (C=O); 1618 (C=N); 1532, 1348 ($NO_2$). Found, %: C 52.58; H 5.71; N 16.25. $C_{19}H_{25}N_5O_7$. Calculated, %: C 52.41; H 5.75; N 16.09.

Compound **VIIf**. Yield 96%, mp 127–128°C. IR spectrum, ν, $cm^{-1}$: 3396 (NH); 1619 (C=N); 1532, 1350 ($NO_2$). Found, %: C 49.81; H 4.65; N 16.53. $C_{14}H_{16}N_4O_6$. Calculated, %: C 50.00; H 4.76; N 16.67.

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