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Synthesis of 5-Substituted 3-(2-Oxopropyl)tetrahydrofuran-2-ones and Heterocyclic Compounds on Their Base

T. V. Kochikyan, E. V. Arutyunyan, V. S. Arutyunyan, and A. A. Avetisyan

Erevan State University, ul. Aleka Manukyana 1, Erevan, 375025 Armenia
e-mail: edgarhar2002@mail.ru

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Abstract—Alkylation of ethyl 2-oxotetrahydrofuran-3-carboxylates with 2,3-dichloroprop-1-ene and 3-bromoprop-1-yne gave new 3,5,5-tri- and 3,3,5,5-tetrasubstituted tetrahydrofuran-2-ones which were converted into the corresponding 3-(2-oxopropyl)tetrahydrofuran-2-ones. Reactions of the latter with semicarabazide, thiosemicarbazide, and phenylhydrazine were studied with a view to obtain new heterocyclic lactones.

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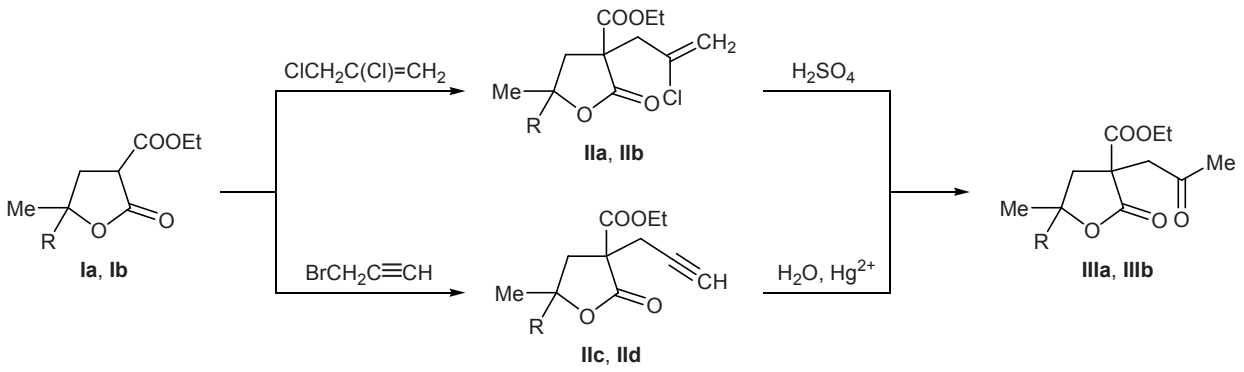
It is known that oxo lactones are convenient starting materials for the synthesis of various heterocyclic compounds. In particular, thiazolyl- and triazolyl-substituted lactones [1, 2] and indolyl lactones possessing cardiovascular activity [3, 4] were prepared, etc.

We have developed a general procedure for the synthesis of 5-substituted 3-(2-oxopropyl)tetrahydrofuran-2-ones **IIIa**–**IIId** starting from ethyl 2-oxotetrahydrofuran-3-carboxylates **Ia** and **Ib** (Scheme 1). Compounds **Ia** and **Ib** are fairly strong heterocyclic CH acids [5–7] and are capable of undergoing alkylation with halogen derivatives. As alkylating agents we used 2,3-dichloroprop-1-ene and 3-bromoprop-1-yne. The alkylation was performed in anhydrous ethanol in the presence of an equimolar amount of sodium ethoxide. The yields of alkylation products **IIa**–**IId** were 80–88%. Compounds **IIa** and **IIb** were subjected to acid hydrolysis, and optimal conditions for the formation of functionally substituted lactones **IIIa** and **IIIb** were found. It is advisable to perform the reaction in concentrated sulfuric acid (96%). At a lower concentration of sulfuric acid, the yield of compounds **IIIa** and **IIIb** decreased as a result of concurrent hydrolysis of the ester moiety. Compounds **IIIa** and **IIIb** were also obtained by the Kucherov hydration of acetylenic derivatives **IIc** and **IId**.

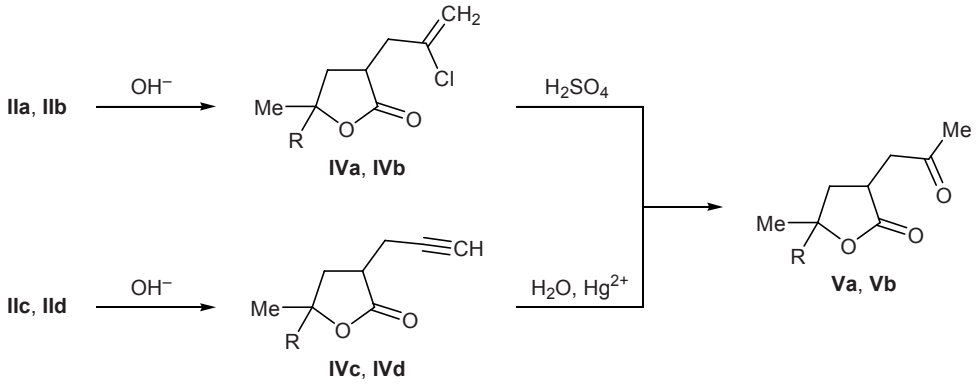
Alkaline hydrolysis of **IIa**–**IId**, followed by decarboxylation, gave 5-substituted 3-oxo-(2-chloroprop-2-en-1-yl)- and -3-(prop-2-yn-1-yl)tetrahydrofuran-2-ones **IVa**–**IVd** in 73–80% yield (Scheme 2). Compounds **IVa**–**IVd** were subjected to hydrolysis according to the procedures described above for **IIa**–**IId**; as a result, 5-substituted 3-(2-oxopropyl)tetrahydrofuran-2-ones **Va** and **Vb** were isolated. Compounds **IIIa**,

Scheme 1.



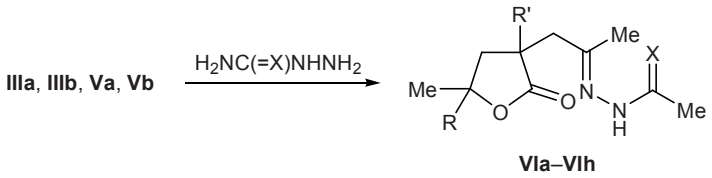
R = H (**a**, **c**), Me (**b**, **d**).

Scheme 2.



R = H (**a**, **c**), Me (**b**, **d**).

Scheme 3.



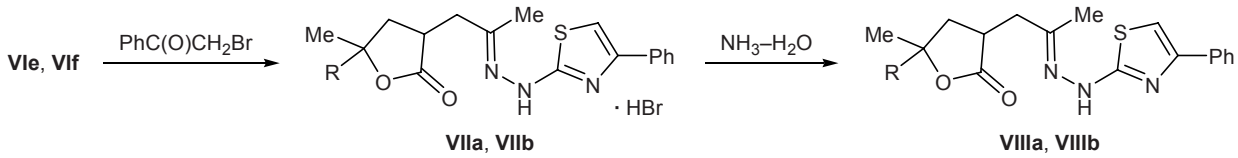
X = O, R = H, R′ = EtOCO (**a**), H (**c**); R = Me, R′ = EtOCO (**b**), H (**d**); X = S, R′ = EtOCO, R = H (**e**), Me (**f**); R′ = H, R = H (**g**), R = Me (**h**).

IIIb, **Va**, and **Vb** readily reacted with semicarbazide and thiosemicarbazide to afford the corresponding semicarbazones and thiosemicarbazones **VIa**–**VIf** (Scheme 3).

Thiosemicarbazones attract interest from the practical viewpoint; it is known that some their analogs exhibit antimutagenic activity [8]; in addition, thiosemicarbazones are convenient reagents for fine organic synthesis. For example, compounds **VIe** and **VIf** smoothly reacted with bromoacetophenone to produce new heterocyclic lactones, (4-phenylthiazol-2-yl)hydrazone hydrobromides **VIIa** and **VIIb**; treatment of the latter with aqueous ammonia gave the corresponding free bases **VIIIa** and **VIIIb** (Scheme 4).

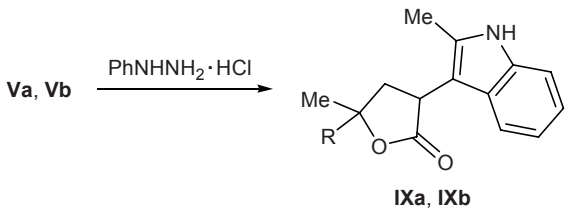
With a view to obtain indole derivatives, compounds **Va** and **Vb** were treated with phenylhydrazine

Scheme 4.



R = H (**a**), Me (**b**).

Scheme 5.



R = H (**a**), Me (**b**).

hydrochloride. As a result, we isolated 70–73% of 5-substituted 3-(2-methyl-1*H*-indol-3-yl)tetrahydrofuran-2-ones **IXa** and **IXb** (Scheme 5). Preliminarily tests showed that indolyl-substituted lactones **IXa** and **IXb** exhibit hypotensive and membrane excitation effects. All the isolated compounds were characterized by physical constants and IR and ^{1}H NMR spectra, and their purity was checked by TLC.

EXPERIMENTAL

The ^{1}H NMR spectra were recorded from solutions in $CDCl_3$ on a Varian Mercury-300 spectrometer (300 MHz). The IR spectra were measured from thin films or suspensions in mineral oil on a Nicolet FTIR NEXUS instrument. Thin-layer chromatography was performed on Silufol UV-254 plates using ethanol–benzene–hexane (3 : 3 : 10, A) or ethanol–benzene (1 : 5, B) as eluent; development with iodine vapor. The melting points were determined on a Boetius melting point apparatus.

Initial ethyl 2-oxotetrahydrofuran-3-carboxylates **Ia** and **Ib** were synthesized according to the procedure described in [9].

Ethyl 5-methyl-2-oxotetrahydrofuran-3-carboxylates IIa–IId (*general procedure*). Lactone **Ia** or **Ib**, 0.5 mol, was added dropwise to a solution of 11.5 g (0.5 mol) of metallic sodium in 400 ml of anhydrous ethanol. The mixture was stirred for 0.5 h, 0.55 mol of 2,3-dichloroprop-1-ene or 3-bromoprop-1-yne was added, and the mixture was stirred for 0.5 h and heated on a water bath until neutral reaction. The solvent was distilled off, and the residue was cooled and acidified to pH 2–3 with dilute hydrochloric acid. The product was extracted into diethyl ether, the extracts were washed with water and dried over anhydrous magnesium sulfate, the solvent was removed, and the residue was distilled under reduced pressure.

Ethyl 3-(2-chloroprop-2-en-1-yl)-5-methyl-2-oxotetrahydrofuran-3-carboxylate (IIa). Yield 80%, bp 109–110°C (1 mm), R_f 0.49 (A), n_D^{20} = 1.4700, d_4^{20} = 1.1745. IR spectrum, ν, cm^{-1}: 1770 (C=O, lactone), 1730 (C=O, ester), 1230 (C–O–C), 1640 (C=C), 3050 (=C–H), 780 (C–Cl). Found, %: C 53.44; H 6.00; Cl 14.21. $C_{11}H_{15}ClO_4$. Calculated, %: C 53.66; H 6.08; Cl 14.40.

Ethyl 3-(2-chloroprop-2-en-1-yl)-5,5-dimethyl-2-oxotetrahydrofuran-3-carboxylate (IIb). Yield 88%, bp 111–112°C (1 mm), R_f 0.48 (A), n_D^{20} = 1.4710, d_4^{20} = 1.1517. The IR spectrum of **IIb** was analogous to that of ester **IIa**. Found, %: C 55.05; H 6.51; Cl 13.48. $C_{12}H_{17}ClO_4$. Calculated, %: C 55.28; H 6.53; Cl 13.63.

Ethyl 5-methyl-2-oxo-3-(prop-2-yn-1-yl)tetrahydrofuran-3-carboxylate (IIc). Yield 83%, bp 94–96°C (1 mm), R_f 0.48 (A), n_D^{20} = 1.4605, d_4^{20} = 1.1063. IR spectrum, ν, cm^{-1}: 1770 (C=O, lactone), 1730 (C=O, ester), 1230 (C–O–C), 2130 (C≡C). Found, %: C 62.66; H 6.70. $C_{11}H_{14}O_4$. Calculated, %: C 62.85; H 6.67.

Ethyl 5,5-dimethyl-2-oxo-3-(prop-2-yn-1-yl)-tetrahydrofuran-3-carboxylate (IId). Yield 85%, bp 97–98°C (1 mm), R_f 0.45 (A), n_D^{20} = 1.4610, d_4^{20} = 1.0852. The IR spectrum of **IId** was analogous to that of **IIc**. Found, %: C 64.00; H 7.10. $C_{12}H_{16}O_4$. Calculated, %: C 64.28; H 7.14.

Ethyl 2-oxo-3-(2-oxopropyl)tetrahydrofuran-3-carboxylates IIIa and IIIb (*general procedure*). Concentrated sulfuric acid (96%), 14 ml, was added dropwise to 0.05 mol of compound **IIa** or **IIb** at such a rate that the temperature did not exceed 20°C. The mixture was stirred until hydrogen chloride no longer evolved (12–13 h), poured into ice water, and extracted with diethyl ether, the extract was washed with water and dried over anhydrous magnesium sulfate, the solvent was removed, and the residue was distilled under reduced pressure. IR spectrum, ν, cm^{-1}: 1775 (C=O, lactone); 1710 (C=O, ketone); 1730 (C=O, ester); 1140, 1180 (C–O–C).

Ethyl 5-methyl-2-oxo-3-(2-oxopropyl)tetrahydrofuran-3-carboxylate (IIIa). Yield 60%, bp 119–120°C (2 mm), R_f 0.45 (A), n_D^{20} = 1.4570, d_4^{20} = 1.1433. Found, %: C 57.75; H 7.00. $C_{11}H_{16}O_5$. Calculated, %: 57.89; H 7.02.

Ethyl 5,5-dimethyl-2-oxo-3-(2-oxopropyl)tetrahydrofuran-3-carboxylate (IIIb). Yield 62%, bp 124°C (2 mm), R_f 0.48 (A), n_D^{20} = 1.4570, d_4^{20} = 1.1840. Found, %: C 59.32; H 7.50. $C_{12}H_{18}O_5$. Calculated, %: C 59.50; H 7.44.

3-Substituted 5-methyltetrahydrofuran-2-ones IVa–IVd (*general procedure*). Compound **IIa**–**IId**, 0.1 mol, was added dropwise to 12 g (0.3 mol) of 30% aqueous sodium hydroxide, and the mixture was stirred for 0.5 h at room temperature and for 2 h on heating on a boiling water bath. The mixture was cooled, acidified to pH 1–2 with concentrated hydrochloric acid, and extracted with diethyl ether, the extract was washed with water and dried over anhydrous magnesium sulfate, the solvent was distilled off, and the residue was subjected to decarboxylation. The product was isolated by vacuum distillation. IR spectrum, ν, cm^{-1}: 1770

(C=O, lactone), 1230 (C–O–C); 1640 (C=C), 3050 (=C–H), 2130 (C≡C), 3280 (≡C–H), 780 (C–Cl).

5-Methyl 3-(2-chloroprop-2-en-1-yl)tetrahydrofuran-2-one (IVa). Yield 80%, bp 75°C (2 mm), R_f 0.47 (A), n_D^{20} = 1.4760, d_4^{20} = 1.1449. Found, %: C 55.00; H 6.30; Cl 20.22. $C_8H_{11}ClO_2$. Calculated, %: C 55.01; H 6.30; Cl 20.34.

3-(2-Chloroprop-2-en-1-yl)-5,5-dimethyltetrahydrofuran-2-one (IVb). Yield 78%, bp 74–75°C (1 mm), R_f 0.46 (A), n_D^{20} = 1.4725, d_4^{20} = 1.1085. Found, %: C 57.07; H 6.91; Cl 18.68. $C_9H_{13}ClO_2$. Calculated, %: C 57.29; H 6.68; Cl 18.83.

5-Methyl-3-(prop-2-yn-1-yl)tetrahydrofuran-2-one (IVc). Yield 73%, bp 69–70°C (1 mm), R_f 0.44 (A), n_D^{20} = 1.4660, d_4^{20} = 1.0491. Found, %: C 69.38; H 7.21. $C_8H_{10}O_2$. Calculated, %: C 69.57; H 7.25.

5,5-Dimethyl-3-(prop-2-yn-1-yl)tetrahydrofuran-2-one (IVd). Yield 75%, bp 97–98°C (2 mm), mp 40–41°C, R_f 0.46 (A). Found, %: C 71.25; H 7.91. $C_9H_{12}O_2$. Calculated, %: C 71.05; H 7.89.

5-Substituted 3-(2-oxopropyl)tetrahydrofuran-2-ones Va and Vb (*general procedure*). Compound **IVc** or **IVd**, 0.1 mol, was added dropwise to a solution of 1.3 g of mercury(II) sulfate in 50 ml of 7% sulfuric acid at such a rate that the temperature did not exceed 35–40°C. The mixture was stirred for 1 h at 20–25°C and for 5 h at 60–65°C, cooled, and extracted with diethyl ether, the extract was washed with water and dried over anhydrous magnesium sulfate, the solvent was removed, and the residue was distilled under reduced pressure.

5-Methyl-3-(2-oxopropyl)tetrahydrofuran-2-one (Va). Yield 73%, bp 94–95°C (1 mm), R_f 0.35 (A), n_D^{20} = 1.4551, d_4^{20} = 1.0992. Found, %: C 61.70; H 7.46. $C_8H_{12}O_3$. Calculated, %: 61.53; H 7.69.

5,5-Dimethyl-3-(2-oxopropyl)tetrahydrofuran-2-one (Vb). Yield 76%, bp 107–108°C (1 mm), R_f 0.41 (A), n_D^{20} = 1.4575, d_4^{20} = 1.0869. Found, %: C 63.75; H 8.10. $C_9H_{14}O_3$. Calculated, %: 63.53; H 8.24.

Semicarbazones VIa–VId (*general procedure*). A mixture of 0.02 mol of ketone, 2.2 g (0.02 mol) of semicarbazide hydrochloride, 3.9 g (0.04 mol) of potassium acetate, and 20 ml of ethanol was heated for 1 h under reflux (on a water bath). The mixture was cooled and diluted with 30 ml of water. The precipitate was filtered off, washed with water, dried, and recrystallized from ethanol.

Ethyl 5-methyl-2-oxo-3-(2-semicarbazonopropyl)tetrahydrofuran-3-carboxylate (VIa). Yield 85%, mp 159–161°C, R_f 0.48 (B). Found, %: C 50.45; H 6.80; N 14.65. $C_{12}H_{19}N_3O_5$. Calculated, %: C 50.53; H 6.67; N 14.74.

Ethyl 5,5-dimethyl-2-oxo-3-(2-semicarbazonopropyl)tetrahydrofuran-3-carboxylate (VIb). Yield 93%, mp 196–198°C, R_f 0.50 (B). Found, %: C 52.30; H 7.15; N 13.86. $C_{13}H_{21}N_3O_5$. Calculated, %: C 52.17; H 7.02; N 14.05.

5-Methyl-3-(2-semicarbazonopropyl)tetrahydrofuran-2-one (VIc). Yield 86%, mp 163–164°C, R_f 0.49 (B). Found, %: C 50.60; H 7.15; N 19.65. $C_9H_{15}N_3O_3$. Calculated, %: C 50.70; H 7.04; N 19.72.

5,5-Dimethyl-3-(2-semicarbazonopropyl)tetrahydrofuran-2-one (VId). Yield 92%, mp 188–189°C, R_f 0.50 (B). IR spectrum, ν, cm^{-1}: 1755 (C=O, lactone); 1180 (C–O–C); 1670 (C=O, amide); 1615 (C=N); 3250, 3175 (NH, NH_2). Found, %: C 52.75; H 7.55; N 18.42. $C_{10}H_{17}N_3O_3$. Calculated, %: C 52.86; H 7.42; N 18.50.

Thiosemicarbazones VIe–VIh (*general procedure*). Two drops of concentrated sulfuric acid were added to a mixture of 40 ml of ethanol, 0.02 mol of the corresponding lactone, 2 g (0.022 mol) of thiosemicarbazide, and 40 ml of water, and the mixture was heated for 1 h on a boiling water bath. The mixture was cooled, and the precipitate was filtered off, washed with water, dried, and recrystallized from aqueous alcohol.

Ethyl 5-methyl-2-oxo-3-(2-thiosemicarbazonopropyl)tetrahydrofuran-3-carboxylate (VIe). Yield 90%, mp 172–174°C, R_f 0.55 (B). Found, %: C 47.95; H 6.20; N 13.72; S 10.45. $C_{12}H_{19}N_3O_4S$. Calculated, %: C 47.84; H 6.31; N 13.95; S 10.63.

Ethyl 5,5-dimethyl-2-oxo-3-(2-thiosemicarbazonopropyl)tetrahydrofuran-3-carboxylate (VIf). Yield 91%, mp 189–191°C, R_f 0.62 (B). Found, %: C 49.40; H 6.80; N 13.05; S 10.00. $C_{13}H_{21}N_3O_4S$. Calculated, %: C 49.52; H 6.67; N 13.33; S 10.16.

5-Methyl-3-(2-thiosemicarbazonopropyl)tetrahydrofuran-2-one (VIg). Yield 81%, mp 153–154°C, R_f 0.50 (B). Found, %: C 46.30; H 6.45; N 18.57; S 13.78. $C_9H_{15}N_3O_2S$. Calculated, %: C 46.16; H 6.55; N 18.34; S 13.98.

5,5-Dimethyl-3-(2-thiosemicarbazonopropyl)-tetrahydrofuran-2-one (VIh). Yield 80%, mp 189–190°C, R_f 0.55 (B). IR spectrum, ν, cm^{-1}: 1755 (C=O, lactone); 1180 (C–O–C); 1615 (C=N); 3250, 3175 (NH, NH_2). Found, %: C 49.50; H 7.15; N 17.67; S 13.44.

$C_{10}H_{17}N_3O_2S$. Calculated, %: C 49.38; H 7.00; N 17.27; S 13.17.

4-Phenylthiazol-2-ylhydrazones VIIIa and VIIIb (*general procedure*). Anhydrous acetone, 15 ml, was added to a mixture of 0.01 mol of thiosemicarbazone **VIe** or **VIf** and 2 g (0.01 mol) of bromoacetophenone. The mixture was stirred for 0.5 h at 20–25°C and for 1 h on heating under reflux, cooled, and diluted with 30 ml of diethyl ether, and the precipitate was filtered off, washed with diethyl ether, and dried. The resulting hydrobromide was placed in a beaker, water was added, and the mixture was adjusted to pH 9–10 by adding aqueous ammonia. The precipitate was filtered off, washed with water, dried, and recrystallized from aqueous alcohol. IR spectrum, ν, cm^{-1}: 1760 (C=O, lactone), 1190 (C–O–C), 1540 (C=N), 1610 (C=C_{arom}), 1640 (C=C), 3200 (NH).

5-Methyl-3-[2-(4-phenyl-1,3-thiazol-2-ylhydrazono)propyl]tetrahydrofuran-2-one (VIIIa). Yield 80%, mp 136–138°C, R_f 0.39 (B). ^{1}H NMR spectrum, δ, ppm: 1.34 s (3H, CH_3), 1.55 m (1H, 3-H), 1.70 t (2H, 3-CH_2), 1.95 s (3H, CH_3), 2.38 d and 2.40 d (1H each, 4-H), 4.53 d.q (1H, 5-H), 6.75 s (1H, 5′-H), 7.15 t (1H, *p*-H), 7.27 t (2H, *m*-H), 7.85 d (2H, *o*-H), 10.50 s (1H, NH). Found, %: C 62.20; H 5.65; N 12.95; S 9.90. $C_{17}H_{19}N_3O_2S$. Calculated, %: C 62.01; H 5.76; N 12.77; S 9.73. **VIIIa**·HBr, mp 192–193°C.

5,5-Dimethyl-3-[2-(4-phenyl-1,3-thiazol-2-ylhydrazono)propyl]tetrahydrofuran-2-one (VIIIb). Yield 82%, mp 154–156°C, R_f 0.38 (B). ^{1}H NMR spectrum, δ, ppm: 1.30 s and 1.45 s (6H, CH_3), 1.68 m (1H, 3-H), 1.74 t (2H, 3-CH_2), 1.97 s (3H, CH_3), 2.32 d and 2.38 d (1H each, 4-H), 6.87 s (1H, 5′-H), 7.21 t (1H, *p*-H), 7.32 t (2H, *m*-H), 7.78 d (2H, *o*-H), 10.53 s (1H, NH). Found, %: C 63.10; H 6.00; N 12.35; S 9.55. $C_{18}H_{21}N_3O_2S$. Calculated, %: C 62.97; H 6.12; N 12.24; S 9.33. **VIIIb**·HBr, mp 197–198°C.

5,5-Dimethyl-3-(2-methyl-1*H*-indol-3-yl)tetrahydrofuran-2-ones IXa and IXb (*general procedure*). A mixture of 0.05 mol of lactone **Va** or **Vb**, 7.2 g (0.05 mol) of phenylhydrazine hydrochloride, 25 ml of anhydrous ethanol, and 3 ml of concentrated sulfuric acid was heated for 2 h on a boiling water bath. The mixture was cooled and diluted with water, and the precipitate was filtered off, washed with water, and dried. IR spectrum, ν, cm^{-1}: 1770 (C=O, lactone); 1140, 1180 (C–O–C); 1630 (C=C_{arom}); 3080 (=C–H); 1610 (C=C_{arom}); 3400 (NH).

5-Methyl-3-(2-methyl-1*H*-indol-3-yl)tetrahydrofuran-2-one (IXa). Yield 70%, mp 72–74°C (from water–alcohol, 2:1), R_f 0.48 (A). ^{1}H NMR spectrum, δ, ppm: 1.38 s and 1.90 s (3H each, CH_3), 2.20–2.80 m (2H, 4-H), 3.08 m (1H, 3-H), 4.53 d.q (1H, 5-H), 7.10–7.30 m (4H, C_6H_4), 9.0 s (1H, NH). Found, %: C 73.50; H 6.25; N 6.25. $C_{14}H_{15}NO_2$. Calculated, %: C 73.36; H 6.55; N 6.11.

5,5-Dimethyl-3-(2-methyl-1*H*-indol-3-yl)tetrahydrofuran-2-one (IXb). Yield 73%, mp 68–70°C (from water–alcohol, 2:1), R_f 0.46 (A). ^{1}H NMR spectrum, δ, ppm: 1.31 s and 1.42 s (3H each, CH_3), 1.85 s (3H, CH_3), 2.34–2.78 m (2H, 4-H), 3.10 m (1H, 3-H), 7.10–7.15 m and 7.25–7.30 m (2H each, C_6H_4), 9.10 s (1H, NH). Found, %: C 73.90; H 7.15; N 5.85. $C_{15}H_{17}NO_2$. Calculated, %: C 74.07; H 7.00; N 5.76.

REFERENCES

1. Kochikyan, T.V., Samvelyan, M.A., Arutyunyan, V.S., and Avetisyan, A.A., *Russ. J. Org. Chem*., 2005, vol. 41, p. 894.
2. Kochikyan, T.V., Arutyunyan, E.V., Arutyunyan, V.S., and Avetisyan, A.A., *Khim. Geterotsikl. Soedin*., 2006, p. 123.
3. Dickel, D.F. and de Stevens, G., US Patent no. 3538223, 1970; *Chem. Abstr*., 1971, vol. 74, no. 22694j.
4. Dickel, D.F. and de Stevens, G., US Patent no. 3686211, 1971; *Chem. Abstr*., 1972, vol. 77, no. 151925w.
5. Kochikyan, T.V., Arutyunyan, E.V., Arutyunyan, V.S., and Avetisyan, A.A., *Russ. J. Org. Chem*., 2003, vol. 39, p. 1140.
6. Kochikyan, T.V., Samvelyan, M.A., Arutyunyan, V.S., and Avetisyan, A.A., *Russ. J. Org. Chem*., 2003, vol. 39, p. 1329.
7. Kochikyan, T.V., Arutyunyan, E.V., Arutyunyan, V.S., and Avetisyan, A.A., *Khim. Zh. Arm*., 2003, vol. 56, no. 4, p. 51.
8. Arutyunyan, V.S., Kochikyan, T.V., Avetisyan, A.A., and Korpakova, I.G., Armenian Patent no. 1114, 2002.
9. Arutyunyan, V.S., Kochikyan, T.V., Arutyunyan, E.V., and Avetisyan, A.A., *Uch. Zap. Erev. Gos. Univ*., 2002, no. 1, p. 73.