Synthesis of heterocyclic systems with carbohydrate fragment
2.* Stereoselective synthesis of tetrahydropyridones by reaction of levoglucosenone with amides of α-methylene-active acids

*A. V. Samet, V. P. Kislyi, N. B. Chernyshova, D. N. Reznikov, B. I. Ugrak, and V. V. Semenov**

N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences,
47 Leninsky prosp., 117913 Moscow, Russian Federation.
Fax: +7 (095) 135 5328

The reactions of levoglucosenone with amides of several α-nitrocarboxylic acids and acetoacetic acid result in tetrahydropyridones fused with a carbohydrate fragment. In the case of acetoacetic acid amides, mixtures of keto and enol tautomers were obtained. The stereochemistry of cyclization is discussed in detail.

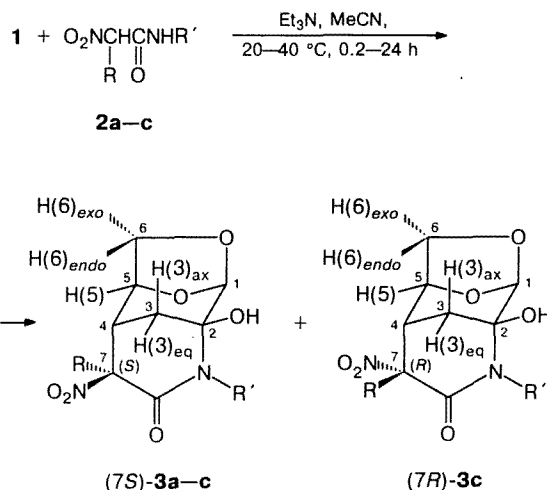**Key words:** levoglucosenone, α-nitrocarboxylic acid amides, acetoacetic acid amides, stereoselective heterocyclization.

The heterocyclization of levoglucosenone (1) with binucleophiles involving its C=C and C=O bonds, which allows syntheses of heterocyclic systems fused with a carbohydrate fragment, is one of the reactions of 1 that has not been studied at all until recently.[2] Similar reactions with the participation of 1,3-binucleophiles are rather widely used for assembling six-membered heterocycles from α,β-unsaturated carbonyl compounds.[3]

In the present work we studied the reaction of compound 1 with amides of α-methylene-active acids, namely, α-nitrocarboxylic acids and acetoacetic acid. Such amides containing an electron-withdrawing substituent (CN, COR, Ar, Ht) at the α-position and, hence, a reactive proton, have found use in syntheses of substituted pyridones and their hydrogenated derivatives.[4−7]
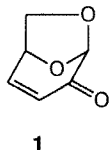
The reactions of nitroacetamide 2a, N-hexylnitroacetamide 2b, and α-nitropropionamide 2c with 1 gave compounds 3a—c (Scheme 1). Conclusive evidence of ring closure lies in the facts that the ^{13}C NMR spectra of compounds 3a—c do not contain a signal of the keto group carbon at δ ~200 typical of products of the addition of carbanions[2] and azoles[1] to levoglucosenone and that a signal of a quaternary carbon atom (C(2)) appears at δ ~80 (Table 1). In addition, some coupling constants and the shapes of some signals in the ^{1}H NMR spectra changed in comparison with those for the addition products (cf. Table 2 and Ref. 1; this will be reported in more detail in the next communication of this series[8]), and the absorption band of the carbonyl group at 1730—1750

cm⁻¹ typical of addition products[1] disappears in the IR spectra.

Of note is the fact that the usually observed elimination of a water molecule from addition products[4−7] does not occur under the reaction conditions. This is probably due to the fact that the OH group in compound 3 is

Scheme 1

3a: R = R′ = H (62 %)
3b: R = H, R′ = (CH₂)₅Me (49 %)
3c: R = Me, R′ = H (69 %) (7S+7R)

---

* For Communication 1, see Ref. 1.

Table 1. ^{13}C NMR spectra $((CD_3)_2CO)$ of compounds **3a—f**, **5d—f**

Com-pound	^{13}C NMR, δ						
	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	Others C atoms
3a	104.09 (d)	82.80 (s)	29.55 (dd)	38.82 (d)	76.26 (d)	68.15 (dd)	87.36 (d, C(7)); 164.19 (s, CO-amide)
3b	101.06 (d)	84.17 (s)	31.25 (dd)	36.23 (d)	75.05 (d)	67.12 (dd)	14.11 (q, CH_3); 22.28, 26.87, 29.03, 29.27, 40.47 (all t, CH_2); 87.06 (d, C(7)); 162.50 (s, CO-amide)
(7C)-**3c**	103.02 (d)	81.45 (s)	28.59 (dd)	41.29 (d)	72.49 (d)	67.19 (dd)	19.99 (q, CH_3); 91.64 (s, C(7)); 166.02 (s, CO-amide)
(7R)-**3c**	102.70 (d)	81.21 (s)	30.71 (dd)	42.79 (d)	73.49 (d)	67.55 (dd)	24.90 (q, CH_3); 91.73 (s, C(7)); 166.66 (s, CO-amide)
3d	103.13 (d)	81.13 (s)	29.48 (dd)	33.91 (d)	76.64 (d)	67.49 (dd)	30.32 (q, CH_3); 58.46 (d, C(7)); 169.60 (s, CO-amide); 205.19 (s, CO-ketone)
3e	101.42 (d)	84.25 (s)	30.25 (dd)	33.46 (d)	77.04 (d)	68.17 (dd)	17.74 (t, CH_2CN); 30.83 (q, CH_3); 36.21 (t, NCH_2); 59.40 (d, C(7)); 118.55 (s, CN); 169.49 (s, CO-amide); 204.16 (s, CO-ketone)
3f	101.69 (d)	84.75 (s)	30.61 (dd)	33.23 (d)	77.27 (d)	67.92 (dd)	30.40 (q, CH_3); 59.48 (d, C(7)); 127.49, 129.18, 130.46, 138.16 (arom.); 169.29 (all s, CO-amide); 205.77 (s, CO-ketone)
5d	103.86 (d)	80.95 (s)	32.34 (dd)	33.79 (d)	77.32 (d)	68.01 (dd)	17.93 (q, CH_3); 99.37 (s, C(7)); 168.17 (s, CO-amide); 173.83 (s, =C—OH)
5e	102.29 (d)	83.73 (s)	32.62 (dd)	33.83 (d)	77.57 (d)	68.44 (dd)	17.85 (t, CH_2CN); 18.18 (q, CH_3); 36.25 (t, NCH_2); 99.08 (s, C(7)); 118.88 (s, CN); 168.76 (s, CO-amide); 173.34 (s, =C—OH)
5f	102.46 (d)	84.75 (s)	32.94 (dd)	33.23 (d)	77.77 (d)	68.32 (dd)	18.13 (q, CH_3); 100.01 (s, C(7)); 127.49, 128.73, 130.32, 137.76 (arom.); 169.21 (all s, CO-amide); 173.60 (s, =C—OH)

located at the head of the bridge, and hence, according to the Bradt rule, the elimination of water is unfavorable.

The tetrahydropyridone ring is closed at the side opposite to the 1,6-anhydro bridge ("from below"), *i.e.*, the same stereochemistry is observed as for nucleophile addition at the C=C bond.[1,2,9] This is confirmed by the values of the coupling constants, $J_{4,3ax} = 3.5 \div 4.2$ Hz and $J_{4,3eq} = 2.5 \div 3.0$ Hz. These relatively low coupling constants suggest the equatorial location of the H(4) proton: if the heterocycle were closed "from atop," the H(4)

atom would be axial, and a higher *trans*-diaxial $J_{4,3ax}$ constant would be observed, which is not the fact.

The reaction of levoglucosenone with amides containing an α-methylene unit (**2a,b**) gave only one of the two possible C(7) epimers (see Scheme 1), which is quite different from the stereochemical result of the addition at the C=C bond.[2] Molecular mechanics calculations of molecule **3a**[10] showed that the dihedral angle H(7)—C(7)—C(4)—H(4) is 43° in the (7R)-epimer and 84° in the (7S)-epimer. Since the signal of the H(7) proton in

Table 2. ^{1}H NMR spectra ($(CD_3)_2CO$) of compounds **3a—f, 5d—f**

Com-pound	|	|	|	|	^{1}H NMR, δ (J/Hz)	|	|	|
	H(1)	H(3)$_{eq}$	H(3)$_{ax}$	H(4)	H(5)	H(6)$_{exo}$	H(6)$_{endo}$	Other H atoms
3a	4.98 (d, $J = 1.8$)	2.24 (ddt, $J = 13.2$, 2.8, 1.8)	2.36 (br.dd, $J = 13.2$, 3.5)	2.83 (dist.q)	4.81 (m)	3.83 (dd, $J = 8.0$, 4.8)	4.15 (d, $J = 8.0$)	5.31 (br.s, H(7)); 5.65—5.85 (br.s); 7.20—7.25 (br.s); (NH, OH)
3b	5.10 (br.s)	2.33—2.38 (m)		2.76 (dist.q)	4.83 (m)	3.82 (dd, $J = 8.0$, 4.8)	4.14 (d, $J = 8.0$)	0.88 (t, CH$_3$); 1.30 (br.s, (CH$_2$)$_4$; 1.52—1.66 (m, CH$_2$); 3.37 (d t, $J = 13.1$, 7.6; NCH$_A$H$_B$); 3.58 (d t, $J = 13.1$, 7.6; NCH$_A$H$_B$); 5.34 (br.s, H(7)); 5.90—6.00 (br.s, OH);
(7C)-3c	4.97 (d, $J = 1.9$)	2.05—2.10 (m)	2.23 (ddd, $J = 13.4$, 3.8, 1.9)	2.61 (dist.q)	4.83 (m)	3.84 (dd, $J = 8.0$, 4.8)	4.13 (d, $J = 8.0$)	1.89 (s, CH$_3$); 5.80—5.88 (br.s); 7.35—7.42 (br.s); (NH, OH)
(7R)-3c	4.98 (d, $J = 1.9$)	2.00—2.05 (m)	2.41 (ddd, $J = 13.4$, 4.2, 1.9)	2.52 (dist.q)	4.23 (m)	3.79 (dd, $J = 8.0$, 4.7)	4.12 (d, $J = 8.0$)	1.94 (s, CH$_3$); 5.71—5.80 (br.s); 7.25—7.32 (br.s); (NH, OH)
3d	4.86 (d, $J = 1.7$)	1.88 (dm, $J = 12.8$)	2.13 (dm, $J = 12.8$)	Overlaps	4.47 (m)	3.72 (dd, $J = 7.7$, 4.7)	4.04 (d, $J = 7.7$)	2.34 (s, CH$_3$); 3.66 (br.s, H(7)); 5.95—6.08 (br.s); 7.00—7.08 (br.s); (NH, OH)
3e	5.09 (d, $J = 1.9$)	Overlaps	2.30 (ddd, $J = 13.0$, 4.1, 1.9)	2.42 (dist.q)	4.53 (m)	3.77 (dd, $J = 7.6$, 4.7)	4.08 (d, $J = 7.6$)	2.34 (s, CH$_3$); 3.49—3.68 (m, NCH$_A$H$_B$); 3.76 (br.s, H(7)); 3.84—3.94 (m, NCH$_A$H$_B$); 5.70—5.80 (br.s, OH)
3f	5.12 (d, $J = 2.0$)	2.23 (dm, $J = 12.9$)	2.38 (ddd, $J = 12.9$, 4.1, 2.0)	2.49 (dist.q)	4.65 (m)	3.82 (dd, $J = 7.6$, 4.7)	4.13 (d, $J = 7.6$)	2.35 (s, CH$_3$); 3.92 (br.s, H(7)); 5.33 (s, OH); 7.10—7.40 (m, Ph)
5d	4.90 (d, $J = 1.8$)	1.61 (ddt, $J = 12.1$, 2.7, 1.8)	Overlaps	2.87 (dist.q)	4.33 (m)	3.73 (dd, $J = 7.6$, 4.6)	4.08 (d, $J = 7.6$)	1.95 (s, CH$_3$); 5.95—6.08 (br.s); 7.00—7.08 (br.s); (NH, OH) 14.92 (s, OH-enol);
5e	5.15 (d, $J = 1.9$)	1.75 (ddt, $J = 12.3$, 2.8, 1.9)	2.47 (dd, $J = 12.3$, 4.0)	2.91 (dist.q)	4.38 (m)	3.77 (dd, $J = 7.6$, 4.7)	4.11 (d, $J = 7.6$)	1.97 (s, CH$_3$); 3.49—3.68 (m, NCH$_A$H$_B$); 3.84—3.94 (m, NCH$_A$H$_B$); 5.70—5.80 (br.s, OH); 14.61 (s, OH-enol)
5f	5.14 (d, $J = 1.9$)	1.97 (ddt, $J = 12.4$, 2.7, 1.9)	2.57 (dd, $J = 12.4$, 4.0)	3.00 (dist.q)	4.50 (m)	3.82 (dd, $J = 7.6$, 4.7)	4.16 (d, $J = 7.6$)	2.01 (s, CH$_3$); 5.37 (s, OH); 7.10—7.40 (m, Ph); 14.84 (s, OH-enol)

the ^{1}H NMR spectrum of compound **3a** (as well as **3b**) is a slightly broadened singlet (*i.e.*, $J_{4,7} \sim 0$), the (7S)-configuration was assigned to the products **3a,b**, in accordance with the well known Carplus dependence.[11] This is also confirmed by the nuclear Overhauser effect (NOE): irradiation of **3a** at the resonance absorption frequency of the H(7) proton results in a noticeable increase (4.7 %) in intensity of the H(5) proton signal.

This can be expected in the (7S)-epimer, in which these protons are in close proximity.

On the other hand, the reaction of compound **1** with α-nitropropionamide **2c** gives a mixture of epimers **3c** in a 4 : 3 ratio. The absolute configurations of the predominating and minor epimers **3c** were also determined by NOE: irradiation of the mixture of isomers **3c** at the frequency of resonance absorption of protons of the Me
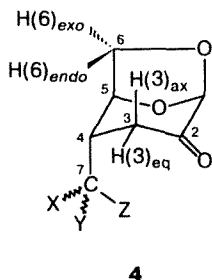
Fig. 1. Structure of molecule **4**.

group in the major epimer (chemical shift 1.89 ppm) disturbs the H(5) signal of this epimer (chemical shift 4.81 ppm). However, irradiation at the frequency of the Me group in the minor epimer (chemical shift 1.94 ppm) does not affect its H(5) signal (chemical shift 4.23 ppm). Thus, it has been established that the major epimer **3d** has a (7*S*)-configuration, while the minor epimer has a (7*R*)-configuration.

We explain the high stereoselectivity of the formation of compounds **3a,b** (unlike in the formation of **3c** and addition of prochiral carbanions[2]) as follows. In type **4** addition products (Fig. 1), the difference in the energy of the epimers becomes insignificant due to the possible free rotation around the C(4)—C(7) bond. In type **3** compounds, ring closure makes free rotation impossible, the structure becomes rigid, and hence there is a reason to expect a higher difference between the energies of C(7) epimers. An important role probably belongs to the repulsion between H(5) and the bulky nitro group located close to it in the (7*R*)-epimer.

It is important to note that the epimerization on treatment with a base to give the thermodynamically more stable isomers **3a,b** is only possible due to the presence of an acid proton H(7) in the molecules of these compounds. The molecule of compound **3c** does not contain a proton at C(7), and hence, epimerization is impossible. Therefore, the stereochemistry at C(7) is kinetically controlled at the addition step, as in the case of the addition of ethyl α-nitropropionate.[2] In view of this, it is not surprising that the stereochemical results are also similar: the epimer ratio in the products of reactions between compound **1** and the ester and amide of α-nitropropionic acid is 4 : 3.

The reactions of the amide, (2-cyanoethyl)amide, and anilide of acetoacetic acid (**2d—f**, respectively) with compound **1** gave mixtures of compounds, which were assigned structures **3d—f** and **5d—f** (Scheme 2).

By analogy with **3a,b**, one could expect a higher thermodynamic stability of (7*R*)-epimers **3d—f** and their predominance in the reaction mixture due to the intramolecular repulsion between the MeCO group and the H(5) proton in (7*S*)-epimers **3d—f**, in which they are in closer proximity. In fact, the H(7) signal in the ¹H NMR spectra of compounds **3d—f** is observed as a slightly broadened singlet (*i.e.*, $J_{4,7} \approx 0$). This agrees with

Scheme 2
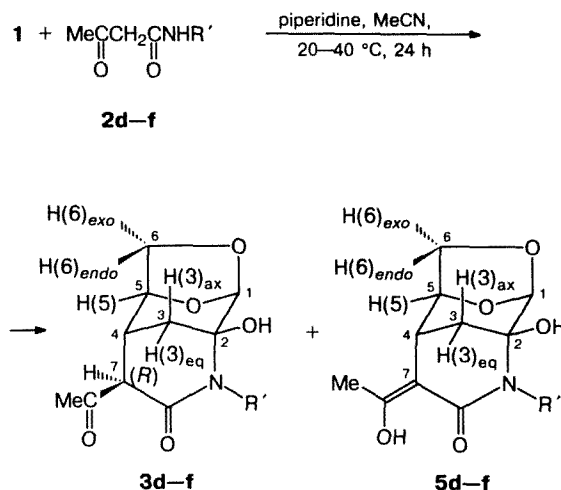
3d, 5d: R′ = H (57 %)
3e, 5e: R′ = CH₂CH₂CN (61 %)
3f, 5f: R′ = Ph (52 %)

the calculated dihedral angle H(7)—C(7)—C(4)—H(4) in the (7*R*)-epimer of **3d** (85°) rather than in the (7*S*)-epimer (41°). (7*S*)-Epimers **3d—f** were not found in the reaction mixture.

The structure of the second components of the mixtures was determined owing to the presence of a very weak-field singlet (δ ~15) in the ¹H NMR spectra of the reaction mixtures. Such signals are typical of enol proton signals with an intramolecular hydrogen bond.[11] In addition, the ¹H NMR spectra of compounds **5** do not contain signals of the H(7) proton and display a characteristic upfield shift of the signals from the methyl group protons (δ 2.3—2.4 in **3d—f** and δ 1.9—2.0 in **5d—f**, where the Me group is adjacent to the C=C bond rather than to the carbonyl group). The upfield shift of the signal from the methyl group carbon is also observed in the ¹³C NMR spectrum (δ ~30 in **3d—f** and δ ~20 in **5d—f**). In addition, along with the signals of the carbonyl group carbon at δ ~205, the ¹³C NMR spectrum of the reaction mixture also contains a signal from quaternary carbon at δ ~173 corresponding to the =C—OH moiety.

The question of the tautomer ratio of compounds **3** and **5** in the mixture is also worthy of attention. For example, the ratio of **3d** and **5d**, 6 h after the crystals obtained by recrystallization of the product of the reaction of **2d** with levoglucosenone were dissolved in deuteroacetone, was found to be 1 : 2 (¹H NMR data). In the course of the reaction between compound **1** and **2f**, the **3f** : **5f** ratio was 1 : 1 30 min after dissolving the crystals in deuteroacetone, 1 : 2 after 48 h, and 2 : 5 after two weeks. The product of the reaction between compounds **1** and **2e** was a yellow oil, which did not crystallize for

two weeks. According to ^{1}H NMR data, it contained a mixture of **3e** and **5e** in 1 : 2 ratio. The composition of the crystals precipitated after two weeks noticeably differed from the oil composition: 2 h after dissolving in deuteroacetone, the **3e** : **5e** ratio was 2 : 1, but it changed to 1 : 2 after 48 h (*i.e.*, it returned to the value observed in the oil).

Thus, the enol form **5** is more thermodynamically stable (at least, at room temperature in deuteroacetone) than the keto form **3**. However, it is likely that the initially formed crystals are enriched with the keto form due to its lower solubility. In solution, keto-enol tautomerization occurs rather slowly, and equilibrium is established in several hours or even days.

Experimental

^{1}H NMR spectra were obtained on a Bruker WM-250 spectrometer with a 250.13 MHz working frequency, ^{13}C NMR spectra on a Bruker AM-300 spectrometer at 75.47 MHz, and IR spectra were recorded in KBr pellets on a Specord M-80 instrument. Products **3a,c—f** (**5d—f**), were recrystallized from MeCN, and compound **3b** was recrystallized from a MeCN—ether (1 : 3) mixture. Elemental analyses of the products gave satisfactory results.

Synthesis of nitroacetamide. Ethyl nitroacetate (39.9 g, 0.3 mol) was added to 11 % aqueous ammonia (250 mL; $d = 0.953$ g mL^{-1}), and the mixture was kept for three days. The solution was acidified to pH 1 and extracted with ether (3×250 mL). The ethereal solution was dried with MgSO$_4$ and concentrated. The yield of **2a** was 25.3 g (81 %).

Using a similar procedure, α-nitropropionamide **2c** (0.81 g, 70 %) was obtained from ethyl α-nitropropionate (1.45 g, 0.01 mol).

Amides of acetoacetic acid (unsubstituted amide **2d**, *N*-(2-cyanoethyl)amide **2e**, and anilide **2f**) were obtained by reactions of ammonia or amines (β-aminopropionitrile, aniline) with diketene.[12]

Synthesis of amides of acetoacetic acid (2d—f). General procedure. An amine (0.01 mol, or, in the case of **2d**, calculated amount of 20 % aqueous ammonia) was added to diketene (0.84 g, 0.01 mol) at 0 °C (for amides **2d** and e) or at 20 °C (for **2f**). The reaction was accompanied with strong heating. 5 min after amine was added, the oils formed were grinded with ether, and crystallization occured (in the case of **2d**, water was first distilled off, and the oil obtained was cooled to 0 °C) to give the amides in quantitative yields in all cases.

The melting points of amides **2a,c—f** correspond with the literature data.[13—15]

Reaction of levoglucosenone with amides of α-methyleneactive acids (2a—f). General procedure. Et$_3$N or piperidine (in the case of acetoacetamides **2d—f**) (10 mol. %, 3—4 drops) was added to a warm (40—50 °C) solution of amide **2** (5 mmol) in MeCN (3 mL), and then compound **1** (5 mmol, 0.63 g) was added dropwise over 30 min (in the case of acetoacetamides **2d—f**, a solution of the same amount of **1** in 5 mL of MeCN was used).

(1*S*,2*R*,5*S*,6*R*,7*S*)-1-Hydroxy-7-nitro-3,11-dioxa-9-azatricyclo[4.3.1.1^{2,5}]undecan-8-one* (3a). 10 min after all the levoglucosenone was added to a solution of nitroacetamide **2a**, the reaction mixture was cooled in a refrigerator to give colorless crystals of compound **5a** (0.71 g, 62 %). M.p. 194—196 °C (dec.). IR, ν/cm^{-1}: 3345, 1690, 1665, 1555.

(1*S*,2*R*,5*S*,6*R*,7*S*)-1-Hydroxy-7-nitro-9-hexyl-3,11-dioxa-9-azatricyclo[4.3.1.1^{2,5}]undecan-8-one (3b). 1 h after all the levoglucosenone was added to a solution of *N*-hexylnitroacetamide **2b**, the reaction mixture was diluted with ether (5 mL). In 5 min compound **3b** precipitated as colorless crystals, yield 0.76 g (49 %). M.p. 158—159 °C (dec.). IR, ν/cm^{-1}: 3310, 1625—1640, 1555, 1375.

(1*S*,2*R*,5*S*,6*R*,7*S*)-1-Hydroxy-7-methyl-7-nitro-3,11-dioxa-9-azatricyclo[4.3.1.1^{2,5}]undecan-8-one and (1*S*,2*R*,5*S*,6*R*,7*R*)-1-hydroxy-7-methyl-7-nitro-3,11-dioxa-9-azatricyclo[4.3.1.1^{2,5}]undecan-8-one (3c). The reaction was carried out using α-nitropropionamide **2c** (0.12 g, 1 mmol), levoglucosenone (1 mmol, 0.13 g), and one drop of Et$_3$N in MeCN (2 mL). After one day, the reaction mixture was cooled in a refrigerator to give colorless crystals of (7*S*)-**3c** (61 mg). The precipitate was filtered off, and the filtrate was concentrated to ~1/3 of the initial volume and again cooled in a refrigerator to give a mixture of (7*R*)-**3c** and (7*S*)-**3c** in a 10 : 7 ratio (92 mg). The filtrate was then evaporated to dryness, and the remaining crystals were washed with ether to give 20 mg of (7*R*)-**3c**. The overall yield of epimer mixture **3c** was 69 %, and the ratio of the (7*S*)- and (7*R*)-epimers was 4 : 3. (7*S*)-**3c**: m.p. 214—216 °C (dec.). IR, ν/cm^{-1}: 3380, 3350, 1675, 1550, 1345. (7*R*)-**3c**: m.p. 209—212 °C (dec.). IR, ν/cm^{-1}: 3380, 3320, 1675, 1555, 1345.

(1*S*,2*R*,5*S*,6*R*,7*R*)-7-Acetyl-1-hydroxy-3,11-dioxa-9-azatricyclo[4.3.1.1^{2,5}]undecan-8-one (3d) and (1*S*,2*R*,5*S*,6*R*)-(7*Z*)-1-hydroxy-7-[(1-hydroxy)ethylidene]-3,11-dioxa-9-azatricyclo[4.3.1.1^{2,5}]undecan-8-one (5d) were obtained from compound **1** and acetoacetamide **2d**. The reaction mixture was kept for 1 day and concentrated, and the residue was crystallized from MeCN. The resulting mixture of tautomers **3d** and **5d** is formed as colorless crystals, overall yield 0.66 g (57 %). IR, ν/cm^{-1}: 3320, 3270, 1715, 1660, 1630.

(1*S*,2*R*,5*S*,6*R*,7*R*)-7-Acetyl-1-hydroxy-9-(2-cyanoethyl)-3,11-dioxa-9-azatricyclo[4.3.1.1^{2,5}]undecan-8-one (3e) and (1*S*,2*R*,5*S*,6*R*)-(7*Z*)-1-hydroxy-7-[(1-hydroxy)ethylidene]-9-(2-cyanoethyl)-3,11-dioxa-9-azatricyclo[4.3.1.1^{2,5}]undecan-8-one (5e) were obtained from compound **1** and *N*-(2-cyanoethyl)amide of acetoacetic acid **2e**. The reaction mixture was treated as above. However, the resulting yellow oil did not crystallize even after passing it through a layer of silica gel. The yield of the mixture of tautomers **3e** and **5e** was 0.85 g (61 %). After two weeks, colorless crystals precipitated. They were mechanically separated and washed with chloroform on a filter. IR, ν/cm^{-1}: 3320, 2260, 1715, 1605—1620.

(1*S*,2*R*,5*S*,6*R*,7*R*)-7-Acetyl-1-hydroxy-9-phenyl-3,11-dioxa-9-azatricyclo[4.3.1.1^{2,5}]undecan-8-one (3f) and (1*S*,2*R*,5*S*,6*R*)-(7*Z*)-1-hydroxy-7-[(1-hydroxy)ethylidene]-9-phenyl-3,11-dioxa-9-azatricyclo[4.3.1.1^{2,5}]undecan-8-one (5f) were obtained by a similar procedure from compound **1** and acetoacetanilide **2f**, but the resulting oil crystallized after the treatment specified above. The yield of tautomers **3f** and **5f** was 0.79 g (52 %). IR, ν/cm^{-1}: 3420, 2900—3060, 1715, 1590—1335.

---

* Systematic nomenclature and corresponding atomic numbering in the names of the compounds are not used anywhere else in this work.

References

1. A. V. Samet, A. L. Laikhter, D. N. Reznikov, A. N. Yamskov, B. I. Ugrak, V. V. Elkin, N. B. Chernysheva, and V. V. Semenov, *Izv. Akad. Nauk, Ser. Khim.*, 1994, 1135 [*Russ. Chem. Bull.*, 1994, **43**, 1073 (Engl. Transl.)].
2. A. V. Samet, A. L. Laikhter, V. P. Kislyi, B. I. Ugrak, and V. V. Semenov, *Mendeleev Commun.*, 1994, 134.
3. V. I. Ivanskii, *Khimiya geterotsiklicheskikh soedinenii*, Vysshaya shkola, Moscow, 1984 (in Russian).
4. E. Kohler and B. Souther, *J. Am. Chem. Soc.*, 1922, **44**, 2903.
5. H. Hammouda, A. El-Reedy, and S. Hussain, *J. Heterocycl. Chem.*, 1986, **23**, 1203.
6. R. Meyer and C. Hauser, *J. Org. Chem.*, 1961, **26**, 3187.
7. K. Sadek, A. Mourad, and A. Abd-Elhaffeez, *Synthesis*, 1983, 739.
8. A. V. Samet, A. N. Yamskov, B. I. Ugrak, L. G. Vorontsova, M. G. Kurella, and V. V. Semenov, *Izv. Akad. Nauk, Ser. Khim.*, 1996, 415 [*Russ. Chem. Bull.*, 1996, **45**, 399 (Engl. Transl.)].
9. M. Essig, *Carbohydr. Res.*, 1986, **156**, 225.
10. T. Clark, *A Handbook of Computational Chemistry*, John Wiley and Sons, 1985.
11. D. Brown, A. Floyd, and M. Sainsbury, *Organic Spectroscopy*, John Wiley and Sons, 1988.
12. *Advances in Organic Chemistry*, **2**, Interscience Publishers, New York—London, 1960.
13. W. Steinkopf, *Ber.*, 1904, **37**, 4623.
14. W. Steinkopf and A. Supan, *Ber.*, 1910, **43**, 3239.
15. T. Kato and M. Sato, *J. Pharm. Soc. Jpn*, 1972, **92**, 1515.