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INVESTIGATION OF THE PRODUCTS OF INTERACTION OF CYCLIC DIKETONES WITH NITROGEN-CONTAINING 1,4-BINUCLEOPHILES

N. N. Kolos, E. N. Yurchenko, V. D. Orlov, S. V. Shishkina, and O. V. Shishkin

The interaction of arylbis(5,5-dimethylcyclohexane-1,3-dion-2-yl)methanes with o-phenylenediamine and o-aminophenol leads to the preparation of 3,3-dimethyl-11-aryl-2,3,4,5,10,11-hexahydrobenzo[b,e]-1,4-diazepin-1-ones and 3,3,6,6-tetramethyl-9-aryl-10-(2-hydroxyphenyl)-2,4,5,7,9-decahydroacridine-1,8-diones respectively. A one-pot method is proposed for the synthesis of derivatives of hexahydrodibenzo[b,e]-1,4-diazepin-1-ones. The structure of the first member of this series was confirmed by X-ray diffraction analysis.

Keywords: *o*-aminophenol, arylbis(5,5-dimethylcyclohexane-1,3-dion-2-yl)methanes, hexahydrodibenzo[*b,e*]-1,4-diazepin-1-ones, decahydroacridine-1,8-diones, dimedone, *o*-phenylenediamine, cyclocondensation.

In cyclic 1,5-diketones the position of the carbonyl groups determines exclusively the ease of their cyclization and makes them as convenient basis for the synthesis of nitrogen-, oxygen-, and sulfur-containing heterocycles [1, 2].

The aim of the present work is the study of the reactivity of the Michael adducts **1a-j** [3, 4], obtained from dimedone and aromatic aldehydes or furfural (adduct **1j**), in relation to the bidentatic nucleophiles *o*-phenylenediamine **2** and *o*-aminophenol **3**. The cyclic tetraketones **1a-j** exist in the enolic form which makes them structurally close to α,β-unsaturated ketones, the reactivity of which in relation to 1,4-dinucleophiles has been studied previously [5, 6].

The electronic character of the substituents in R influence the direction of the interaction of compounds **1a-i** with *o*-phenylenediamine **2** on boiling these reactants in 2-propanol (method A). The corresponding hexahydrodibenzodiazepinones **4a-f** were obtained from tetraketones **1a** (R = Ph) and **1b-f** (electron-withdrawing substituents in R: 4-F, 4-Cl, 4-Br, 4-NO_2).

When electron-donating substituents (4-OMe, 4-NMe_2, 2-OH) are present in R, as in compounds **1g-i,** either decomposition of the latter takes place (in the case of tetraketones **1g,h**) with the formation of the corresponding azomethines **5a,b**, or conversion into decahydroacridinedione **6** occurs (from tetraketone **1i**). Hexahydrodibenzodiazepinone **4j** is obtained from hetaryl-substituted tetraketone **1j** (R = 2-furyl).

Tetraketones **1a-d,g,h** do not react with *o*-aminophenol **3** under the conditions mentioned above (method A). Only on boiling these reactants in DMF the interaction products, decahydroacridinediones **7a-f**, were obtained in good yield.

The results obtained enable the interaction of compounds **1** with binucleophiles **2** and **3** to be represented in the following way.

Kharkov V. N. Karazin National University, Kharkov 61077, Ukraine; e-mail: orlov@univer.kharkov.ua. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 12, pp. 1798-1808, December, 2004. Original article submitted November 5, 2002; revision submitted February 5, 2004.

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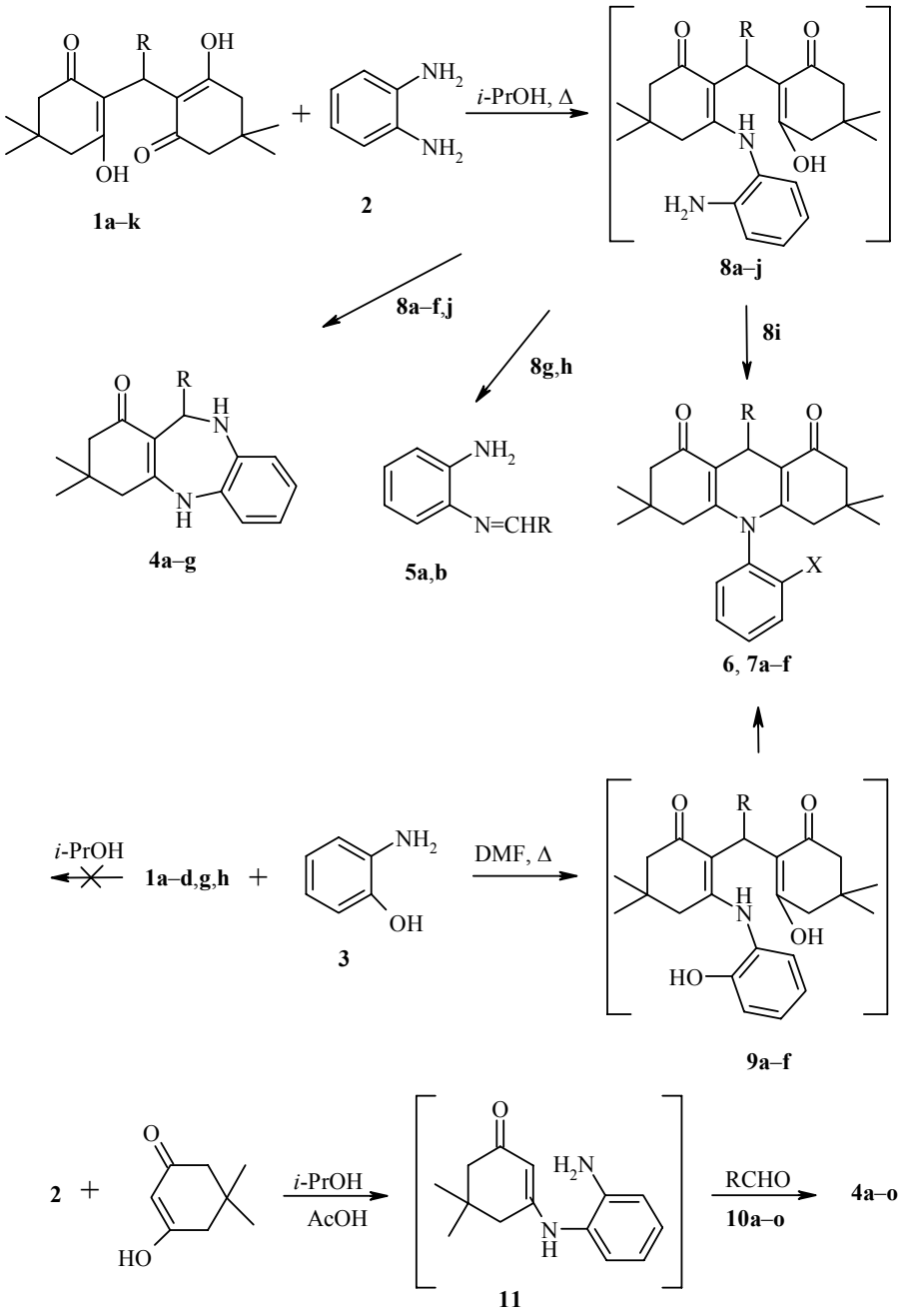

1, **4**, **7-10 a** R = Ph, **b** R = 4-FC_6H_4, **c** R = 4-ClC_6H_4, **d** R = 4-BrC_6H_4;
1, **4**, **8**, **10 e** R = 4-$O_2NC_6H_4$, **f** R = 3-$O_2NC_6H_4$, **g** R = 4-$MeOC_6H_4$, **h** R = 4-$Me_2NC_6H_4$,
i R = 2-HOC_6H_4, **j** R = 2-furyl; **4**, **10 k** R = 2-HO-3-$MeOC_6H_3$, **l** R = 2-thienyl,
m R = 2-(5-nitrothienyl), **n** R = PhCO, **o** R = 4-$O_2NC_6H_4CO$; **5a**, **7e**, **9e** R = 4-$MeOC_6H_4$;
5b, **7f**, **9f** R = 4-$Me_2NC_6H_4$; **6** X = NH_2; **7a–f** X = OH

The formation of products of type **4, 6, 7** includes a stage of nucleophilic addition at the β-position of an enone system in which the amino group of compounds **2** and **3** participates. Subsequent conversion of the intermediate enamines **8** and **9** may proceed by two routes. The first includes nucleophilic attack of the sp^3-hybrid center of the primary amino group with elimination of a molecule of dimedone, while the second is attack at the activated vinylene bond by the electron pair of the enamine nitrogen atom with the formation of the

acridine nucleus. The presence of substituents increasing the partial positive charge on the sp^3-hybrid center aids the formation of the diazepine ring. The formation of acridones is a consequence of reduction of the charge at the sp^3-hybrid carbon atom (synthesis of product **6**) or the low nucleophilicity of the neighboring nucleophilic center (synthesis of products **7a-f**).

Under the conditions of an one-pot synthesis using *o*-phenylenediamine, dimedone, and aldehydes **10a-o** the sole products were hexahydrobenzodiazepinones **4**. Compounds **4a-o** were synthesized on boiling dimedone with diamine **2** in 2-propanol for 30-40 min in the presence of catalytic amounts of AcOH and subsequent addition of aromatic aldehyde **10a-o** to the reaction mixture (method B). Diazepines **4g-i,** containing electron-donating groups in R, and also products **4n,o** with a substituent ArCO at position 11 (the appropriate glyoxals were put into the reaction mixture in place of aldehydes) were obtained by the same method. Compounds **4a-o** were obtained in better yield under conditions of the one-pot synthesis (Table 1), and the reaction time was reduced significantly (see Experimental). The intermediate enamine **11** was not isolated by us under these conditions but its presence has been confirmed as a fact in [7]. The formation of enamine determines the direction of the overall process, since in experiments with simultaneous participation of diamine **2**, dimedone, and aromatic aldehyde **10**, 2-arylbenzimidazoles were obtained exclusively, i.e. the rate of interaction of diamine with aldehyde was greater than the rate of enamine formation, which is in good agreement with our data [8]. The composition and structure of compounds **4a-o**, **6**, **7a-f** were confirmed by data of elemental analysis, IR and ^{1}H NMR spectra (Tables 1 and 2), and in the case of compound **4a**, also by X-ray diffraction analysis (Fig. 1 and Tables 3-5).

According to the data of X-ray diffraction analysis product **4a** is 3,3-dimethyl-11-phenyl-2,3,4,5,10,11-hexahydrodibenzo[*b,e*]-1,4-diazepin-1-one. In the independent part of the unit cell of the compound **4a** crystal there are two molecules (I and II) which differ in the conformation of the cyclohexene fragment. The six-membered ring in molecule I has the form of a distorted chair. The deviations of the C(8) and C(9) atoms from the mean square plane of the remaining ring atoms are 0.52 and 0.13 Å respectively.

In molecule II the cyclohexene fragment is in the *sofa* conformation. The deviation of the C(8') atom from the mean square plane of the remaining ring atoms is 0.65 Å.

The diazepine ring in both molecules has a shape intermediate between a *twist-chair* and a *twist-boat*. The deviations of the N(2) and C(13) atoms from the mean square plane of the remaining ring atoms are 0.84 and 0.22 Å for molecule I and 1.01 and 0.55 Å for molecule II respectively.

The phenyl substituent at C(12) atom (Fig. 1) has an axial orientation [the torsion angle C(6)–C(11)–C(12)–C(16) is 96.2(2)° in molecule I and 84.1(2)° in molecule II] and is twisted relative to the C(11)–C(12) bond [the torsion angle C(11)–C(12)–C(16)–C(21) is 44.9(3)° in molecule I and 29.4(3)° in molecule II].

The formation of intermolecular hydrogen bond N(1')–H(1N')···O(1) (1 - *x*, *y* - 0.5, 0.5 - *z*) (H'···O is 2.11Å, N'–H'···O 169°) leads to lengthening of bonds O(1)–C(10) 1.253(2) (I), 1.254(2) (II), C(6)–C(11) 1.384(3) (I), 1.394(3) Å in (II) and shortening of bond C(10)–C(11) 1.448(3) Å (I), 1.439(3) Å (II) in comparison with mean values of 1.210, 1.340, and 1.464 Å respectively. Shortened contacts were detected in the structure at O(1)···H(12) of 2.36 (I) and 2.33 Å (II), H(15B)···C(10) 2.83 (I) and 2.81 (II), and H(15B')···C(6') 2.77 Å for total sum of the van der Waals radii of O···H 2.45 and H···C 2.87 Å.

The closeness of the spectral characteristics of compounds **4a** and **4b-o** (see Tables 1, 2) permits their assignment to one series of isomers. In their IR spectra there are bands for the stretching vibrations of the enamine carbonyl group of low intensity at 1615-1650 cm^{-1}, and also two bands at 3230-3350 cm^{-1} assigned to the stretching vibrations of the secondary amino group.

The ^{1}H NMR spectra of compounds **4** were more informative. The position, shape, and intensity of the recorded proton signals correspond to the structure of hexahydrodibenzodiazepinones indicated in the scheme (Table 2). The singlets in the region of 6.0 and 8.50 ppm, disappearing under deuterium exchange conditions, were assigned to the imine and enamine protons respectively.

TABLE 1. Characteristics of Compounds **4, 6, 7**

Compound	Empirical formula	Found N, % / Calculated N, %	mp, °C	IR spectrum, ν, cm^{-1}		Yield, % (method)
				C=O	NH	
4a	$C_{21}H_{22}N_2O$	8.29 / 8.81	251-252	1628	3318, 3292	65 (A), 70 (B)
4b	$C_{21}H_{21}FN_2O$	8.30 / 8.33	237-239	1608	3245, 3303	55 (A), 63 (B)
4c	$C_{21}H_{21}ClN_2O$	8.18 / 7.94	239-240	1620	3288, 3233	71 (A), 74 (B)
4d	$C_{21}H_{21}BrN_2O$	7.35 / 7.05	241-242	1638	3235, 3303	60 (A), 64 (B)
4e	$C_{21}H_{21}N_3O_3$	12.00 / 11.57	274-275	1627	3353, 3280	80 (A), 86 (B)
4f	$C_{21}H_{21}N_3O_3$	11.44 / 11.57	144-146	1635	3235, 3315	70 (A), 73 (B)
4g	$C_{22}H_{24}N_2O_2$	8.12 / 8.04	203-205	1615	3246, 3315	60 (B)
4h	$C_{23}H_{27}N_3O$	11.01 / 11.63	228-230	1640	3240, 3310	64 (B)
4i	$C_{21}H_{22}N_2O_2$	8.20 / 8.38	164-166	1650	3250, 3305	70 (B)
4j	$C_{22}H_{24}N_2O_3$	7.99 / 7.69	216-218	1630	3236, 3303	68 (B)
4k	$C_{19}H_{20}N_2O_2$	9.19 / 9.09	269-270	1622	3350, 3285	52 (A), 60 (B)
4l	$C_{19}H_{20}N_2OS$	8.69 / 8.64	227-229	1635	3265, 3303	62 (B)
4m	$C_{19}H_{19}N_3O_3S$	11.76 / 11.38	243-245	1635	3285, 3347	68 (B)
4n	$C_{22}H_{22}N_2O_2$	8.34 / 8.09	233-234	1678	3360, 3303	75 (B)
4o	$C_{22}H_{21}N_3O_4$	10.84 / 10.74	210-212	1675	3370, 3320	65 (B)
6	$C_{29}H_{32}N_2O_3$	5.96 / 6.14	205-206	1620, 1648	3465, 3370	60 (A)
7a	$C_{29}H_{31}NO_3$	3.00 / 3.17	244-246	1622, 1649	3610	64
7b	$C_{29}H_{30}FNO_3$	2.95 / 3.05	298-300	1620, 1642	3610	65
7c	$C_{29}H_{30}ClNO_3$	3.15 / 2.94	286-288	1622, 1643	3610	67
7d	$C_{29}H_{20}BrNO_3$	2.89 / 2.69	283-284	1625, 1640	3610	65
7e	$C_{30}H_{33}NO_4$	2.91 / 2.97	260-262	1620, 1645	3610	72
7f	$C_{31}H_{36}N_2O_3$	5.54 / 5.78	290-291	1624, 1650	3612	68

Product **6** differs significantly in spectral characteristics from the compounds of type **4** considered above. In its ^1H NMR spectrum (Table 2) the proton signals of the methylene and methyl groups have double intensity, there were not two protons subjected to deuterium exchange as in **4** (δ 6.00 and 8.50 ppm), but three. The two-proton signal is found at high field (δ 3.93 ppm) and the one-proton signal – at low field (9.42 ppm). The first signal refers to the NH_2 group, and the second to OH (enolic form). There were also significant differences in the IR spectrum of compound **6**. Two intense carbonyl group absorption bands were observed at 1620-1650 cm^{-1}, and also bands for a primary amino group in the range of 3350-3470 cm^{-1}. All this confirms the structure of product **6** as 3,3,6,6-tetramethyl-9-(2-hydroxyphenyl)-10-(2-aminophenyl)-2,4,5,7,9-decahydro-acridine-1,8-dione.

TABLE 2. ^{1}H NMR Spectral Characteristics of the Synthesized Compounds

Com-pound	Chemical shifts, δ, ppm (SSCC, *J*, Hz)								
	CH_3, s (ΣH)	CH_3, s (ΣH)	$C_{(4)}H_2$ ($1H_A$, d, $1H_B$, d, J = 16.0)	$C_{(2)}H_2$ (2H, d, J = 16.2)	$N_{(10)}H$ (1H, s)	$N_{(5)}H$ (1H, s)	$C_{(11)}H$ (s or $C_{(9)}H$) (ΣH)	OH, NH_2, OCH_3 $N(CH_3)_2$, s (OCH_3)	H_{arom}, m (ΣH)
1	2	3	4	5	6	7	8	9	10
4a	1.08 (3)	1.14 (3)	2.10, 2.18	2.56	6.17	8.75	5.65 (1)		6.55-7.25 (9)
4b	1.03 (3)	1.07 (3)	2.03, 2.20	2.60	6.07	8.70	5.65 (1)		6.49-7.16 (8)
4c*	1.07 (3)	1.15 (3)	2.10, 2.20	2.55	4.39	6.72	5.90 (1)		6.40-7.10
4d	1.03 (3)	1.08 (3)	2.04, 2.22	2.50	6.03	8.63	5.63 (1)		6.42-7.25 (8)
4e	1.08 (3)	1.15 (3)	2.10, 2.20	2.58	6.36	8.96	5.77 (1)		6.52-8.00 (8)
4f	1.05 (3)	1.17 (3)	2.03, 2.24	2.60	6.21	8.75	5.80 (1)		6.45-8.00 (8)
4g	1.05 (3)	1.11 (3)	2.05, 2.20	2.56	5.90	8.55	5.65 (1)	3.66 (3)	6.49-7.39 (8)
4h	1.01 (3)	1.05 (3)	2.05, 2.15	2.54	5.98	8.61	5.55 (1)	2.52 (6)	6.40-6.93 (8)
4i	1.05 (3)	1.10 (3)	2.04, 2.19	2.55	5.85	8.75	5.30 (1)	9.63 (1)	6.39-6.91 (8)
4k	1.05 (3)	1.11 (3)	2.03, 2.20	2.70	5.85	8.70	5.50	8.95 (1), 3.62 (3)	6.16-6.93 (7)
4j*	1.09 (3)	1.17 (3)	2.02, 2.16	2.62	4.43	6.75	5.10 (1)		6.20-7.15 (7)

TABLE 2 (continued)

1	2	3	4	5	6	7	8	9	10
4l	1.01 (3)	1.04 (3)	2.05, 2.21	2.50	6.10	8.70	5.90 (1)		6.60-7.09 (7)
4m	1.02 (3)	1.05 (3)	2.04, 2.24	2.58	6.40	8.92	5.91 (1)		6.68-7.05 (6)
4n	0.88 (3)	1.35 (3)	2.02, 2.18	2.50	6.17	8.84	6.17 (1)		6.40-7.95 (9)
4o	0.84 (3)	1.05 (3)	2.00, 2.19	2.55	6.22	8.90	6.17 (1)		6.49-8.37 (8)
6	0.88 (6)	0.98 (6)	—*[2]	2.24 (4H, s)			5.28 (1)	3.93 (2), 9.42 (1)	6.77-7.26 (8)
7a	0.68 (3), 0.87 (3)	0.72 (6)	1.60-2.20 (8H, m)				5.03 (0.5), 4.93 (0.5)	10.45 (0.5), 10.34 (0.5)	7.00-7.54 (9)
7b	0.70 (6)	0.87 (6)	1.70-2.20 (8H, m)				4.99 (1)	9.99 (1)	6.93-7.27 (8)
7c	0.68 (3), 0.87 (3)	0.73 (6)	1.70-2.20 (8H, m)				5.01 (0.5), 4.91 (0.5)	10.45 (0.5), 10.34 (0.5)	6.95-7.52 (8)
7d	0.70 (3), 0.87 (3)	0.73 (6)	1.70-2.20 (8H, m)				5.01 (0.5), 4.91 (0.5)	10.43 (0.5), 10.33 (0.5)	7.00-7.45 (8)
7e	0.68 (3), 0.87 (3)	0.72 (6)	1.65-2.20 (8H, m)				4.88 (1)	10.40 (1), 3.69 (3)	6.95-7.45 (8)
7f	0.69 (3), 0.87 (3)	0.72 (6)	1.60-2.10 (8H, m)				4.85 (0.5), 4.95 (0.5)	10.20 (0.5), 10.27 (0.5), 2.80 (6)	6.50-7.38 (8)

* Spectra were measured in $CDCl_3$ (compounds **4c,j** and **6**) and DMSO-d_6 (remaining compounds).

*[2] δ, ppm: 1.83 (2H, d, J = 18), 2.19 (2H, d, J = 18).

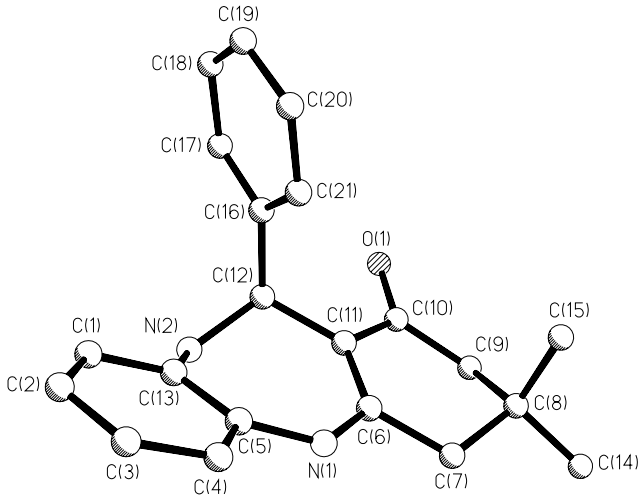

Fig. 1. Structure of the Compound **4a** Molecule.

The considered spectra have much in common with the analogous spectra of products **7a-f** obtained on boiling aminophenol **3** with compounds **1a-d,g,h** in DMF. In addition, there are absorption bands for hydroxyl groups at 3610 cm^{-1} in the IR spectra of products **7a-f**. On this basis the indicated compounds **7a-f** were assigned the structure of decahydroacridine-1,8-diones containing an *o*-hydroxyphenyl group at position 10.

In the ^1H NMR spectra of compounds **7a,c,e,f** at room temperature doubling of the signals of protons of the H-9 methine group and of hydroxyl group was observed, linked evidently with the development of atropoisomerism caused by restriction of rotation around the N–Ar bond and by the presence of an *ortho* substituent in the aromatic nucleus. The ratio of rotamers in **7** proved to be close to 1:1. Doubling of the signals was not recorded in the spectrum of compound **7b** containing *p*-fluorophenyl substituent in position 9, nor in compound **6** having *ortho*-substituted aryl radicals in positions 9 and 10.

TABLE 3. Bond Lengths (*l*) in the Compound **4a** Molecule

Bond	*l*, Å	Bond	*l*, Å	Bond	*l*, Å
O(1)–C(10)	1.253(2)	C(4')–C(5')	1.397(3)	C(11)–C(12)	1.513(3)
N(1)–C(5)	1.413(3)	C(6')–C(11')	1.394(3)	C(16)–C(17)	1.390(3)
N(2)–C(12)	1.487(3)	C(7')–C(8')	1.537(3)	C(17)–C(18)	1.389(4)
C(1)–C(13)	1.395(3)	C(8')–C(9')	1.534(3)	C(19)–C(20)	1.380(4)
C(3)–C(4)	1.386(3)	C(9')–C(10')	1.520(3)	O(1')–C(10')	1.254(2)
C(5)–C(13)	1.401(3)	C(11')–C(12')	1.511(3)	N(1')–C(5')	1.419(2)
C(6)–C(7)	1.513(3)	C(16')–C(21')	1.386(3)	N(2')–C(12')	1.487(3)
C(8)–C(9)	1.524(3)	C(17')–C(18')	1.389(4)	C(1')–C(13')	1.393(3)
C(8)–C(14)	1.541(3)	C(19')–C(20')	1.372(4)	C(3')–C(4')	1.383(3)
C(10)–C(11)	1.448(3)	N(1)–C(6)	1.368(2)	C(5')–C(13')	1.404(3)
C(12)–C(16)	1.531(3)	N(2)–C(13)	1.411(3)	C(6')–C(7')	1.512(3)
C(16)–C(21)	1.390(3)	C(1)–C(2)	1.386(3)	C(8')–C(15')	1.529(4)
C(18)–C(19)	1.378(4)	C(2)–C(3)	1.384(3)	C(8')–C(14')	1.534(3)
C(20)–C(21)	1.386(3)	C(4)–C(5)	1.393(3)	C(10')–C(11')	1.439(3)
N(1')–C(6')	1.365(2)	C(6)–C(11)	1.384(3)	C(12')–C(16')	1.531(3)
N(2')–C(13')	1.402(2)	C(7)–C(8)	1.535(3)	C(16')–C(17')	1.395(3)
C(1')–C(2')	1.384(3)	C(8)–C(15)	1.528(3)	C(18')–C(19')	1.375(4)
C(2')–C(3')	1.381(3)	C(9)–C(10)	1.514(3)	C(20')–C(21')	1.399(3)

TABLE 4. Bond Angles (ω) in Structure **4a**

Angle	ω, deg.	Angle	ω, deg.
C(6)–N(1)–C(5)	133.4(2)	C(13)–N(2)–C(12)	119.6(2)
C(2)–C(1)–C(13)	122.0(2)	C(3)–C(2)–C(1)	119.9(2)
C(2)–C(3)–C(4)	118.7(2)	C(3)–C(4)–C(5)	122.0(2)
C(4)–C(5)–C(13)	119.4(2)	C(4)–C(5)–N(1)	116.4(2)
C(13)–C(5)–N(1)	124.2(2)	N(1)–C(6)–C(11)	126.9(2)
N(1)–C(6)–C(7)	111.3(2)	C(11)–C(6)–C(7)	121.8(2)
C(6)–C(7)–C(8)	115.7(2)	C(9)–C(8)–C(15)	110.7(2)
C(9)–C(8)–C(7)	107.5(2)	C(15)–C(8)–C(7)	110.4(2)
C(9)–C(8)–C(14)	110.0(2)	C(15)–C(8)–C(14)	109.4(2)
C(7)–C(8)-C(14)	108.8(2)	C(10)–C(9)–C(8)	114.4(2)
O(1)–C(10)–C(11)	121.4(2)	O(1)–C(10)–C(9)	119.1(2)
C(11)–C(10)–C(9)	119.4(2)	C(6)–C(11)–C(10)	119.3(2)
C(6)–C(11)–C(12)	126.1(2)	C(10)–C(11)–C(12)	114.6(2)
N(2)–C(12)–C(11)	113.0(2)	N(2)–C(12)–C(16)	110.8(2)
C(11)–C(12)–C(16)	115.5(2)	C(1)–C(13)–C(5)	118.0(2)
C(1)–C(13)–N(2)	120.7(2)	C(5)–C(13)–N(2)	121.2(2)
C(17)–C(16)–C(21)	118.0(2)	C(17)–C(16)–C(12)	118.8(2)
C(21)–C(16)–C(12)	123.1(2)	C(18)–C(17)–C(16)	120.9(3)
C(19)–C(18)–C(17)	120.4(2)	C(18)–C(19)–C(20)	119.2(2)
C(19)–C(20)–C(21)	120.6(3)	C(20)–C(21)–C(16)	120.8(2)
C(6')–N(1')–C(5')	132.9(2)	C(13')–N(2')–C(12')	115.3(2)
C(2')–C(1')–C(13')	121.6(2)	C(3')–C(2')–C(1')	119.7(2)
C(2')–C(3')–C(4')	119.7(2)	C(3')–C(4')–C(5')	121.2(2)
C(4')–C(5')–C(13')	119.2(2)	C(4')–C(5')–N(1')	117.1(2)
C(13')–C(5')–N(1')	123.6(2)	N(1')–C(6')–C(11')	125.9(2)
N(1')–C(6')–C(7')	113.4(2)	C(11')–C(6')–C(7')	120.7(2)
C(6')–C(7')–C(8')	113.7(2)	C(15')–C(8')–C(9')	110.3(2)
C(15')–C(8')–C(14')	110.5(2)	C(9')–C(8')–C(14')	109.7(2)
C(15')–C(8')–C(7')	110.3(2)	C(9')–C(8')–C(7')	106.9(2)
C(14')–C(8')–C(7')	109.0(2)	C(9')–C(8')–C(7')	114.9(2)
O(1')–C(10')–C(11')	121.9(2)	C(10')–C(9')–C(8')	118.2(2)
C(11')–C(10')–C(9')	119.9(2)	O(1')–C(10')–C(9')	119.8(2)
C(6')–C(11')–C(12')	122.6(2)	C(10')–C(11')–C(12')	117.3(2)
N(2')–C(12')–C(11')	111.2(2)	N(2')–C(12')–C(16')	110.9(2)
C(11')–C(12')–C(16')	115.9(2)	C(1')–C(13')–N(2')	121.0(2)
C(1')–C(13')–C(5')	118.6(2)	N(2')–C(13')–C(5')	120.4(2)
C(21')–C(16')–C(17')	117.6(2)	C(21')–C(16')–C(12')	123.2(2)
C(17')–C(16')–C(12')	119.0(2)	C(18')–C(17')–C(16')	121.4(2)
C(19')–C(18')–C(17')	119.7(2)	C(20')–C(19')–C(18')	120.3(3)
C(19')–C(20')–C(21')	119.8(3)	C(16')–C(21')–C(20')	121.1(2)

EXPERIMENTAL

The IR spectra were taken on a Specord IR 75 instrument for KBr disks and solutions in $CHCl_3$ (ν_{OH} for compounds **7a-f**). The ^1H NMR spectra were obtained on a Varian VXR 200 (200 MHz) in DMSO-D_6 and $CDCl_3$, internal standard was TMS.

The purity of compounds was checked by TLC on Silufol UV 254 plates, eluent was chloroform.

X-Ray Investigation of Compound 4a. Crystals of compound **4a** are monoclinic, $C_{21}H_{22}N_2O$, at 20°C: a = 10.666(4), b = 13.214(6), c = 25.098(10) Å; β = 92.82°; V = 3533(3) Å^3, M_r = 318.41, Z = 8, space group $P2_1/c$, d_{calc} = 1.197 g/cm^3, μ(MoKα) = 0.074 mm^{-1}, F(000) = 1360. The unit cell parameters and the intensities of 6531 reflections were measured on a Siemens automatic P3/PC 4-circle diffractometer (MoKα, graphite

TABLE 5. Coordinates (x - 10^4, y - 10^4, z - 10^4) of the Nonhydrogen Atoms in Structure **4a**

Atom	x	y	z	Atom	x	y	z
O(1)	5588(2)	5387(1)	2097(1)	C(7')	5712(2)	-1249(2)	1951(1)
N(1)	4202(2)	4022(1)	393(1)	C(8')	7004(2)	-1515(2)	1744(1)
N(2)	3707(2)	6126(1)	680(1)	C(9')	6766(2)	-2141(2)	1235(1)
C(1)	1864(2)	6052(2)	67(1)	C(10')	5824(2)	-1682(2)	829(1)
C(2)	1136(2)	5576(2)	-331(1)	C(11')	4883(2)	-992(2)	1001(1)
C(3)	1417(2)	4596(2)	-479(1)	C(12')	4056(2)	-487(2)	574(1)
C(4)	2430(2)	4113(2)	-223(1)	C(13')	3098(2)	956(1)	1005(1)
C(5)	3176(2)	4587(2)	174(1)	C(14')	7734(3)	-2151(2)	2166(1)
C(6)	4931(2)	4100(2)	855(1)	C(15')	7728(2)	-550(2)	1623(1)
C(7)	5912(2)	3272(2)	894(1)	C(16')	2735(2)	-930(2)	484(1)
C(8)	6429(2)	3018(2)	1460(1)	C(17')	2098(2)	-793(2)	-9(1)
C(9)	6743(2)	4016(2)	1741(1)	C(18')	854(3)	-1087(2)	-95(1)
C(10)	5687(2)	4783(2)	1717(1)	C(19')	233(3)	-1531(2)	312(1)
C(11)	4846(2)	4830(2)	1247(1)	C(20')	841(2)	-1696(2)	799(1)
C(12)	3965(2)	5728(2)	1229(1)	C(21')	2092(2)	-1394(2)	884(1)
C(13)	2906(2)	5584(2)	319(1)	C(1')	2201(2)	1674(2)	845(1)
C(14)	7627(2)	2377(2)	1420(1)	C(2')	1285(2)	1988(2)	1180(1)
C(15)	5460(2)	2424(2)	1761(1)	C(3')	1238(2)	1572(2)	1684(1)
C(16)	2741(2)	5582(2)	1514(1)	C(4')	2135(2)	873(2)	1855(1)
C(17)	2292(2)	6376(2)	1814(1)	C(5')	3083(2)	569(2)	1526(1)
C(18)	1136(3)	6311(2)	2044(1)	C(6')	4839(2)	-744(2)	1504(1)
C(19)	410(3)	5453(3)	1978(1)	O(1')	5910(2)	-1913(1)	348(1)
C(20)	859(2)	4651(2)	1692(1)	N(1')	4033(2)	-71(1)	1754(1)
C(21)	2011(2)	4713(2)	1461(1)	N(2')	4001(2)	626(1)	657(1)

monochromator, 2θ/θ scanning, $2\theta_{max}$ = 50°). The structure was solved by the direct method with the SHELXL-97 program set [10]. The positions of the hydrogen atoms were calculated geometrically and refined with a rider model with $U_{iso} = nU_{eq}$ of the non-hydrogen atom linked with a given hydrogen atom (n = 1.5 for methyl groups and 1.2 for the remainder). The structure was refined according to F^2 by a full-matrix least-squares method in an anisotropic approach to wR_2 = 0.139 on 6183 reflections [R_1 = 0.050 on 3608 reflections with $F > 4\sigma(F)$, S = 0.976].

3,3-Dimethyl-11-phenyl-2,3,4,5,10,11-hexahydrodibenzo[*b,e*]-1,4-diazepin-1-one (4a). A. Tetraketone **1a** (1.84 g, 5 mmol) and *o*-phenylenediamine (0.54 g, 5 mmol) were boiled in 2-propanol (20 ml) for 5 h. The reaction mixture was cooled, the precipitated solid was filtered off, and crystallized from 50% aqueous ethanol.

Diazepines **4b-f,j** were obtained analogously from tetraketones **1b-f,j** on boiling for 1-10 h (check by TLC), also acridinedione **6** from compound **1i**, and azomethines **5a** (40% yield) and **5b** (45% yield) from compounds **1g,h**. Compound **5a** had mp 101°C (101-102°C [9]), compound **5b** had mp 146°C (147°C [9]).

11-(4-Methoxyphenyl)-3,3-dimethyl-2,3,4,5,10,11-hexahydrodibenzo[*b,e*]-1,4-diazepin-1-one (4g). B. Compound **2** (0.54 g, 5 mmol) and dimedone (0.7 g, 5 mmol) were boiled in ethanol (10 ml) with acetic acid (2-3 drops) for 40 min, then anisaldehyde (**10g**) (5 mmol) was added, and the mixture boiled for 1 h further. After cooling, the precipitated product was filtered off, and crystallized from 50% aqueous ethanol.

Compounds 4a-f,h-o were obtained analogously from aldehydes **10a-f,h-o**. The boiling time after adding aldehyde was from 20 min to 1 h (check by TLC).

10-(2-Hydroxyphenyl)-3,3,6,6-tetramethyl-9-phenyl-2,4,5,7,9-decahydroacridine-1,8-dione (7a). Solution containing compound **1a** (0.74 g, 2 mmol) and amine **3** (0.22 g, 2 mmol) in DMF (10 ml) was boiled for 1 h. After cooling, water (5 ml) was added to the reaction mixture. The precipitate of product was filtered off, and compound **7a** (0.56 g) was obtained.

Compounds 7b-f were obtained analogously from tetraketones **1b-d,g,h.**

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