TABLE 1. Chemical Shifts of ^{13}C (ppm) in 2,3,4,4a,9,9a-Hexahydroindeno[2,1-b]-1,4-oxazines*

R	$C_{(2)}$		$C_{(3)}$		$C_{(4a)}$		$C_{(9a)}$		$C_{(9)}$	
	cis	trans	cis	trans	cis	trans	cis	trans	cis	trans
H	66,5	68,5	40,7	45,9	60,8	65,5	77,9	84,4	37,8	34,2
p-C_4H_9	63,3	67,9	47,6	54,2	66,6	71,3	76,8	83,7	36,3	34,9
$CH(CH_3)_2$	64,7	68,8	43,1	44,5	63,0	64,7	77,8	84,7	35,9	34,8
Cyclohexyl	64,7	68,6	43,5	46,3	62,7	63,7	77,5	84,5	36,3	34,5

*Solutions in $CDCl_3$, internal standard TMS.

Thus, indenoxazines of type I, isolated during the synthesis described earlier [1], represent a mixture of cis- and trans-isomers with substantial predominance of the former.

LITERATURE CITED

1. K. P. Iordanova, N. P. Danchev, and V. I. Shvedov, Khim.-Farm. Zh., No. 5, 552 (1982).
2. H. Booth and Y. Griffts, J. Chem. Soc. Perkin Trans. II, No. 6, 842 (1973).
3. G. Levy and G. Nelson, Carbon-13 Nuclear Magnetic Resonance for Organic Chemists, Wiley (1972).
4. J. Emsley, J. Finney and L. Sutcliffe, High-Resolution NMR Spectroscopy, Pergamon Press (1965).
5. V. F. Zakharov, V. P. Zvolinskii, D. A. Fesenko, and N. S. Prostakov, Zh. Strukt. Khim., 15, 774 (1974).
6. V. F. Zakharov, V. P. Zvolinskii, D. A. Fesenko, and N. S. Prostakov, Zh. Strukt. Khim., 16, 470 (1975).

2-[HYDROXY(DIALKYL)METHYL]-4-ARYL-6,6-DISUBSTITUTED 4,5-DIHYDRO-6H-1,3,4-OXADIAZINONES-5

V. A. Glushkov and I. S. Berdinskii

UDC 547.875

The reactions of arylhydrazides of dialkylglycolic acids with chlorides of α-halocarboxylic acids, followed by cyclization, yielded 2-[hydroxy(dialkyl)methyl]-4-aryl-6,6-disubstituted 4,5-dihydro-6H,1,3,4-oxadiazinones-5.

It is known that halides of α-halocarboxylic acids react with amides, forming 4(5H)-oxazolines [1], while with hydrazides they give derivatives of 4,5-dihydro-6H-1,3,4-oxadiazinone-5 [2]. It is interesting to study arylhydrazides of dialkylglycolic acids, which have a more complex acid residue, in this reaction. However, experiments showed that the formation of a seven-membered ring with attack at the hydroxy group is not observed, and the reaction proceeds analogously to the conversion of the phenylhydrazide of acetic acid [2] with the formation of 2-[hydroxy(dialkyl)methyl]-4-aryl-6,6-disubstituted 4,5-dihydro-6H-1,3,4-oxadiazinone-5 (IVa-m). Such a course of the reaction is explained by the negative inductive effect of the carbonyl groups, as well as by the preferential formation of a six-membered ring:

In the acid chloride IIa the mobility of the α-chlorine atom is so great that the intermediate acyl derivative cannot be isolated, and substances IVa-k are formed immediately when compounds Ia-k and IIa are boiled in benzene. Compounds IVl and IVm are formed from the corresponding acyl derivatives IIIb, when they are boiled in anhydrous acetone with potassium carbonate [2]. The synthesized compounds are presented in Table 1. They are colorless crystalline substances (with the exception of IV*l*), insoluble in water, readily soluble in alcohol,

---

A. M. Gor'kii Perm' State University, Perm' 614600. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 7, pp. 896-897, July, 1984. Original article submitted May 25, 1983; revision submitted November 2, 1983.

0009-3122/84/2007-0726$08.50

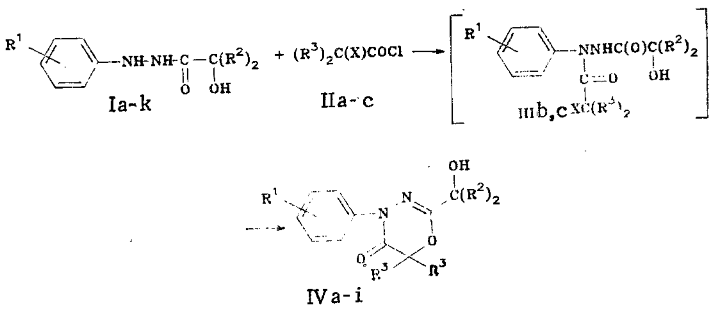
TABLE 1. Characteristics of the Compounds Obtained

Compound	mp, °C[a]	IR spectrum, ν, cm⁻¹			PMR spectrum, δ, ppm	Found, %			Gross formula	Calculated, %			Yield, %
		O–H	C=O	C=N	O–H[b]	C	H	N		C	H	N	
IVa	142–143	3460	1690	1650	2,57	74,9	6,8	6,3	$C_{26}H_{26}N_2O_3$	75,3	6,3	6,7	68
IVb	138–139	3500	1690	1670	2,84	75,7	6,7	6,3	$C_{28}H_{30}N_2O_3$	76,0	6,8	6,3	52
IVc	134–135	3500	1695	1660	2,78	76,8	7,5	5,8	$C_{30}H_{34}N_2O_3$	76,6	7,3	6,0	78
IVd	94–95	3550	1700	1670	2,78	77,1	7,3	5,9	$C_{32}H_{38}N_2O_3$	77,1	7,7	5,6	43
IVe	74–75	3500	1700	1680	2,79	78,1	8,5	5,0	$C_{36}H_{46}N_2O_3$	77,9	8,4	5,1	44
IVf	145–146	3540	1700	1670	2,75	76,4	7,4	5,5	$C_{31}H_{36}N_2O_3$	76,8	7,5	5,8	42
IVg	112–113	3550	1695	1660	2,75	76,7	7,5	5,8	$C_{31}H_{36}N_2O_3$	76,8	7,5	5,8	54
IVh	108–109	3550	1690	1670	2,52	73,6	6,9	5,6	$C_{30}H_{33}FN_2O_3$	73,7	6,8	5,7	34
IVi	115–117	3530	1690	1660	2,65	71,0	6,8	5,6	$C_{30}H_{33}ClN_2O_3$	[illegible]	6,6	5,5	41
IVj	120–121	3525	1690	1675	2,77	65,6	6,1	4,9	$C_{30}H_{33}BrN_2O_3$	65,6	6,0	5,1	31
IVk	98–99	3530	1685	1650	2,88	74,2	7,5	5,4	$C_{31}H_{36}N_2O_4$	74,3	7,2	5,6	46
IVl	Oil[c]	3500	1680	1650	2,97	69,4	8,8	8,1	$C_{20}H_{30}N_2O_3$	69,3	8,7	8,1	80
IVm	30–31	3500	1680	1660	2,88	67,7	8,5	8,7	$C_{18}H_{26}N_2O_3$	67,9	8,2	8,8	36

---

[a] Compounds IVa, g were recrystallized from toluene, the rest from the hexane. [b] In CH_2Cl_2. [c] $d_{20}^{4} = 1.0545$, $n_D^{20} = 1.5166$. Found: MR 99.392. Calculated: MR 98.554.

benzene, chloroform, and ether. Their structure was confirmed by the data of the IR and PMR spectra.



I, IV a $R^1=H$, $R^2=C_2H_5$, $R^3=C_6H_5$; b $R^1=H$, $R^2=C_3H_7$, $R^3=C_6H_5$; c $R^1=H$, $R^2=C_4H_9$, $R^3=C_6H_5$; d $R^1=H$, $R^2=iso\text{-}C_5H_{11}$, $R^3=C_6H_5$; e $R^1=H$, $R^2=n\text{-}C_7H_{15}$, $R^3=C_6H_5$; f $R^1=3\text{-}CH_3$, $R^2=C_4H_9$, $R^3=C_6H_5$; g $R^1=4\text{-}CH_3$, $R^2=C_4H_9$, $R^3=C_6H_5$; h $R^1=4\text{-}F$, $R^2=C_4H_9$, $R^3=C_6H_5$; i $R^1=4\text{-}Cl$, $R^2=C_4H_9$, $R^3=C_6H_5$; j $R^1=4\text{-}Br$, $R^2=C_4H_9$, $R^3=C_6H_5$; k $R^1=4\text{-}CH_3O$, $R^2=C_4H_9$, $R^3=C_6H_5$; l $R^1=H$, $R^2=C_4H_9$, $R^3=CH_3$; m $R^1=H$, $R^2=C_4H_9$, $R^3=H$, II a $R^3=C_6H_5$, X=Cl; b $R^3=CH_3$, X=Br, c $R^3=H$, X=Cl; IIIb $R^3=CH_3$; c $R^3=H$

EXPERIMENTAL

The IR spectra were recorded on an IKS-22 instrument in liquid petrolatum paste. The PMR spectra were recorded for 10% solutions in CCl_4 on a Telsa BS-487C instrument (80 MHz), internal standard HMDS. Acetone (very special purity) for the synthesis of compounds IVl and IVm was used without additional purification.

2-[Hydroxy(diheptyl)methyl]-4,6,6-triphenyl-4,5-dihydro-6H-1,3,4-oxadiazinone-5 (IVe). A mixture of 4.20 g (11.6 mmoles) of the phenyl hydrazide of diheptylglycolic acid [4] and 3.18 g (12 mmoles) of α-chloro-α,α-diphenylacetyl chloride in 80 ml of absolute benzene was heated for 2 h, cooled, washed with water, and with a saturated solution of sodium bicarbonate, dried with sodium sulfate, the solvent evaporated, the residue chromatographed on silica gel (eluent: benzene), and crystallized from pentane. Yield 2.47 g (44%), mp 74-75°C.

Substances IVa-d, f-k were produced analogously.

β-(α'-Bromoisobutyryl)-β-phenylhydrazide of Dibutylglycolic Acid (IIIb). A mixture of 14.0 g (50.3 mmoles) phenylhydrazide of dibutylglycolic acid and 10.0 g (51 mmoles) of α-bromoisobutyryl chloride in 100 ml of benzene was heated for 1 h, then after two days 13.94 g (66%) of substance IIIb, mp 127-128°C (from isopropanol), was filtered off. IR spectrum: 3470 (OH), 3340 (NH), 1680 ($C_6H_5\underset{|}{N}-CO$), 1640 cm⁻¹ (C=O). PMR spectrum of (CF_3COOH): 1.61 (6H, s, $2CH_3$), 7.00-7.55 (5H, m, aromatic protons). Found: C 56.2; H 7.3; N 6.6%. $C_{20}H_{31}BrN_2O_3$. Calculated: C 56.2; H 7.3; N 6.6%.

2-[Hydroxy(dibutyl)methyl]-4-phenyl-4,5-dihydro-6H-1,3,4-oxadiazinone-5 (IVm). A mixture of 2.0 g (5.5 mmoles) of the β-chloroacetyl-β-phenylhydrazide of dibutylglycolic acid [5] and 2.07 g (15 mmoles) of powdered calcined potassium carbonate in 100 ml of acetone was boiled for 15 h. After filtration the solvent was removed and the substance isolated analogously to compound IVe. Yield 0.65 g (36.0%), mp 30-31°C (pentane). PMR spectrum: 2.88 (1H, s, OH); 4.50 (2H, s, CH_2O); 7.00-7.75 (5H, m, aromatic protons). Compound IV*l* was produced analogously. In the PMR spectrum the signals of the two methyl groups in position 6 of the ring appear at 1.50 ppm.

LITERATURE CITED

1. J. S. Rao and R. Filler, Chem. Commun., 1622 (1970).
2. J. von Alphen, Rec. Trav. Chim., 48, 163 (1929).
3. I. S. Berdinskii, Zh. Obshch. Khim., 28, 1263 (1958).
4. I. S. Berdinskii and L. N. Krovnikova, Khim. Geterotsikl. Soedin., No. 2, 220 (1967).
5. I. S. Berdinskii, Zh. Obshch. Khim., 34, 762 (1964).

CONFIGURATIONALLY AND CONFORMATIONALLY HOMOGENEOUS ARYL-cis-1-THIADECALINS

S. K. Klimenko, T. V. Stolbova, T. I. Tyrina,
N. N. Sorokin, I. F. Leshcheva, N. M. Sergeev,
and V. G. Kharchenko

UDC 547.818:542.634:543.422.25

The structure of aryl-substituted cis-1-thiadecalins formed together with 5,6-tetramethylenethiopyrylium salts in disproportionation reactions of condensed 4H-, 6H-thiopyrans and dihydrothiopyrans with CF_3COOH, as well as in the ionic reduction of the latter by the ion pair trifluoroacetic acid–triethylsilane, was studied. It was shown that the reduction proceeds stereospecifically with the formation of configurationally and conformationally homogeneous aryl-cis-1-thiadecalins possessing 2α-R^1- and 2α-R^1-4α-R^2-configurations. The configurational and conformational assignments were made by the ^{13}C NMR method.

Intermolecular hydride transfer in such an acid-catalyzed reaction as the disproportionation of chromenes, thiochromenes, and dihydroquinolines leads to the formation not only of salts but also of products of reduction of the double bond in the heterocycle [1-6]. The stereochemical direction of the processes of reduction of heterocyclic compounds during disproportionation have been rather widely discussed in the literature [1-6]. 3,4-Diaklyl-2H-thiochromenes and N-methyl-1,2-dihydroquinolines are reduced predominantly to cis-isomers under the conditions of the reaction described, while O-analogs form cis- and trans-isomers in equal amounts under analogous conditions [1-6]. Derivatives of 3,4-trimethylene-1,2-dihydroquinoline give only cis-3,4-trimethylenetetrahydroquinoline [2], while 3,4-tetramethylene-2H-thiochromene and chromene are converted in this case 77 and 65%, respectively, to the cis-isomers [3]. Up to 83% cis-isomers are also obtained in the disproportionation of N-methyl-2,3-trimethylene-1,4-dihydroquinolines [5]. Only cis-2,4-diphenylchroman was isolated in disproportionation of 2,4-diphenyl-4H-chromene with CF_3COOH, CF_3COOD, or $HClO_4$ [6]. On the contrary, N-methyl-2,3-$(CH_2)_n$-1,4-dihydroquinolines (n = 4-6) are reduced exclusively or predominantly to trans-N-methyl-2,3-$(CH_2)_n$-1,2,3,4-tetrahydroquinolines [5]. We have shown that in the disproportionation of 2-diphenyl-5,6-tetramethylene-4H-thiopyran or -6H-thiopyran with trifluoroacetic adid, 2,4-diphenyl-cis-1-thiadecalin, which has a cis-cis-cis-configuration, are formed [7-9].

The present investigation was undertaken in order to establish the configuration and conformation of aryl-substituted 1-thiadecalins, which, together with the salt, are disproportionation products of 5,6-tetramethylene-4H(6H)-thiopyrans and dihydrothiopyrans [10-14]. This seems especially important since in the disproportionation of the objects described, two

---

N. G. Chernyshevskii Saratov State University, Saratov 410601. M. V. Lomonosov State University, Moscow 117234. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 7, pp. 898-904, July, 1984. Original article submitted April 6, 1983.

0009-3122/84/2007-0728$08.50