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Stereochemistry of Dihydroxylation of *N*-Arylbicyclo[2.2.1]-hept-5-ene-*endo*- and -*exo*-2,3-dicarboximides

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Abstract—Stereochemistry of the oxidation of *N*-arylbicyclo[2.2.1]hept-5-ene-*endo*- and -*exo*-2,3-dicarboximides at the double bond with peroxyacetic acid generated *in situ* in the presence of sulfuric acid and with an anhydrous dioxane solution of peroxyacetic acid was studied. In both cases, the reaction was stereospecific, regardless of the substituent in the *N*-aryl group and configuration of the imide ring, but the reaction direction depended on the presence of water in the system. In the first case, the corresponding *trans*-5,6-dihydroxy derivatives were formed, while in the second, *exo*-5,6-epoxy derivatives. The oxidation of *N*-arylbicyclo[2.2.1]-hept-5-ene-*endo*- and -*exo*-2,3-dicarboximides with a solution of potassium permanganate in aqueous acetone gave the corresponding *N*-aryl-*cis*-5,6-dihydroxybicyclo[2.2.1]heptane-*endo*- and -*exo*-2,3-dicarboximides. The *exo,cis,exo* and *exo,cis,endo* configurations of the synthesized compounds were determined by ^{1}H NMR spectroscopy.

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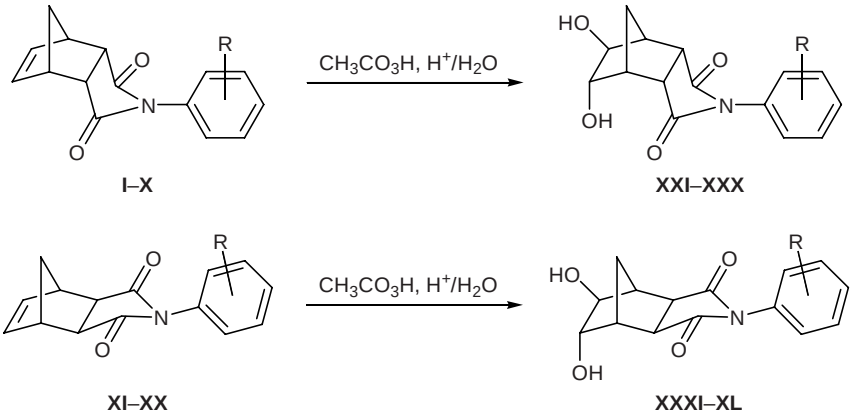
It is known [1–3] that the rate and stereochemistry of addition reactions at the double bond of norbornene derivatives strongly depend on the nature of *endo* and *exo* substituents in positions *2* and *3*. We previously showed [4] that oxidation of bicyclo[2.2.1]hept-5-ene-*endo*- and -*exo*-2,3-dicarboxylic anhydrides at the endocyclic double bond with an anhydrous solution of peroxyacetic acid in dioxane is strictly stereoselective. The observed *exo*-stereoselectivity is determined [5] by strong steric shielding of the double bond by the cyclohexene ring having a *boat*-like conformation, as compared to the effect of the *exo*-methylene bridge. If hydrogen atoms in the methylene bridge of the norbornene fragment are replaced by methyl groups, steric effect of the *syn*-CH_3 groups forces the oxidation with peroxy acids to occur at the opposite side to produce the corresponding *endo*-epoxy derivatives [6]. However, the available data are insufficient to rationalize

Scheme 1.



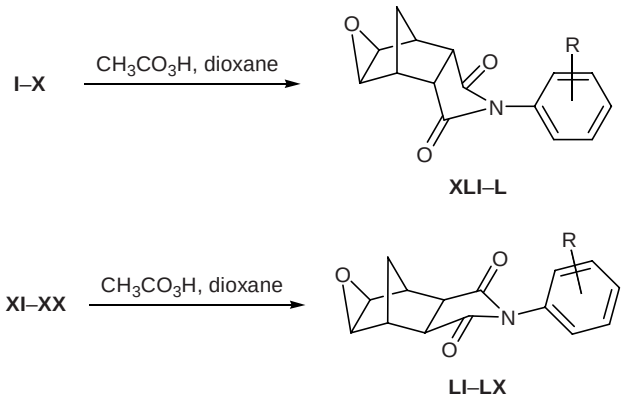
I, **XI**, **XXI**, **XXXI**, R = H; **II**, **XII**, **XXII**, **XXXII**, R = *o*-MeO; **III**, **XIII**, **XXIII**, **XXXIII**, R = *m*-MeO; R = **IV**, **XIV**, **XXIV**, **XXXIV**, *p*-MeO; **V**, **XV**, **XXV**, **XXXV**, R = *o*-Cl; **VI**, **XVI**, **XXVI**, **XXXVI**, R = *m*-Cl; **VII**, **XVII**, **XXVII**, **XXXVII**, R = *p*-Cl; **VIII**, **XVIII**, **XXVIII**, **XXXVIII**, R = *o*-HOCO; **IX**, **XIX**, **XXIX**, **XXXIX**, R = *m*-HOCO; **X**, **XX**, **XXX**, **XL**, R = *p*-HOCO.

the effect of substituent configuration in positions *2* and *3* on the reactivity of *N*-arylbicyclo[2.2.1]hept-5-ene-*endo*- and -*exo*-2,3-dicarboximides **I**–**XX**.

In the present work we studied stereochemical relations holding in the oxidation of *N*-arylbicyclo-[2.2.1]hept-5-ene-*endo*- and -*exo*-2,3-dicarboximides **I**–**XX** at the double bond with peroxyacetic acid generated *in situ* from acetic acid and 30% hydrogen peroxide in the presence of a catalytic amount of sulfuric acid. We anticipated formation of stable epoxy derivatives, taking into account that negative inductive effect (*–I*) of the imide carbonyl groups should favor stabilization of the epoxide ring [7]. However, regardless of the substituent in the *N*-aryl group and imide ring configuration, the oxidation of imides **I**–**XX** at room temperature led to the formation of the corresponding *trans*-dihydroxy imides **XXI**–**XL** [8] (Scheme 1). This means that, in contrast to the data of [9, 10], the initially formed epoxide ring undergoes fast opening.

On the other hand, the oxidation of compounds **I**–**XX** with anhydrous peroxyacetic acid in dioxane gave *exo*-epoxy derivatives **XLI**–**LX** as the only products (Scheme 2). Their acid hydrolysis in aqueous medium leads to *trans*-dihydroxy compounds **XXI**–**XL**, regardless of the configuration of the imide ring and the nature and position of substituent in the aromatic ring. Thus the main factors determining the direction of oxidation of *endo*- and *exo*-imides **I**–**XX** with peroxy acids are the reaction medium and substrate structure.

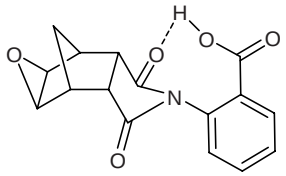
Scheme 2.



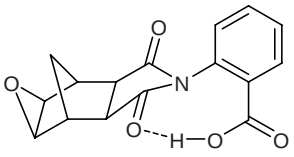
XLI, **LI**, R = H; **XLII**, **LII**, R = *o*-MeO; **XLIII**, **LIII**, R = *m*-MeO; R = **XLIV**, **LIV**, *p*-MeO; **XLV**, **LV**, R = *o*-Cl; **XLVI**, **LVI**, R = *m*-Cl; **XLVII**, **LVII**, R = *p*-Cl; **XLVIII**, **LVIII**, R = *o*-HOCO; **XLIX**, **LIX**, R = *m*-HOCO; **L**, **LX**, R = *p*-HOCO.

Epoxidation of *N*-arylimides **I**–**XX** is stereoselective. Electrophilic oxygen atom approaches the double bond from the side of the *endo*-methylene bridge, regardless of *endo* or *exo* configuration of the imide fragment. Negative inductive effect of the imide fragment is sufficient to stabilize both epoxide ring and norbornane skeleton, for the process is not accompanied by Wagner–Meerwein rearrangement [11].

The presence of a proton-donor carboxy group in the *N*-aryl substituent of compounds **VIII** and **XVIII** does not affect the stability of the oxirane ring and stereochemistry of epoxidation. A probable reason is formation of intramolecular hydrogen bond between strongly electronegative imide carbonyl oxygen atom and hydroxy proton of the carboxy group in *ortho* isomers **XLVIII** and **LVIII**. The carboxy group in *para* isomers **X** and **XX** is unlikely to be involved in such intramolecular hydrogen bond.



XLVIII



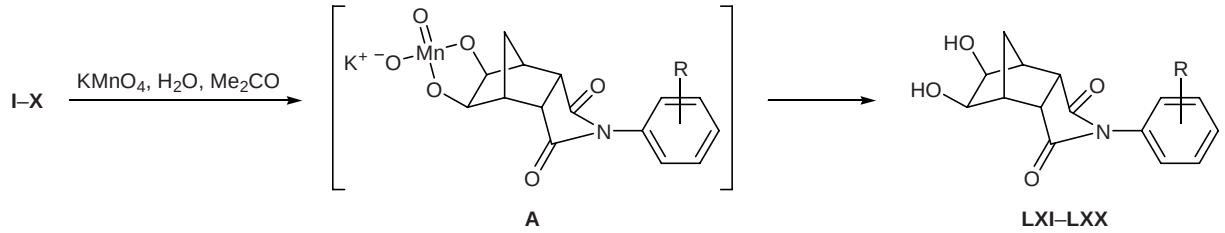
LVIII

The oxidation of imides **I**–**X** with a dilute solution of potassium permanganate in aqueous acetone (neutral medium) at 10°C was strictly stereoselective, and the products were exclusively the corresponding *cis*-dihydroxy derivatives **LXI**–**LXX** with *exo*-oriented hydroxy groups (Scheme 3). Thus, either *cis*- or *trans*-dihydroxy imides can be obtained, depending on the conditions.

The *trans* configuration of the hydroxy groups in diols **XXI**–**XL** was proved by the presence in their IR spectra of an absorption band at 3620 cm^{-1}, which is typical of stretching vibrations of free hydroxy groups [12]. *cis*-Diols **LXI**–**LXX** displayed bands at 3465, 3480, and 3405 cm^{-1}, which characterize hydroxy groups involved in intramolecular hydrogen bond.

The steric structure of the obtained compounds was confirmed by analysis of their ^1H NMR spectra [13]. Protons in the bridging methylene group (*syn*-7-H and *anti*-7-H) resonate as a doublet of doublets at δ 1.25–1.75 ppm (*AB* spin system, ^2J = 10 Hz). The *syn*-7-H proton in *endo*-dihydroxy derivatives **XXI**–**XXX** shows additional long-range *W*-coupling [14, 15] with 2-H and 3-H. Its signal is a broadened doublet ($W_{1/2}$ = 5 Hz) located in a weaker field relative to the *anti*-7-H

Scheme 3.



LXI, R = H; **LXII**, R = *o*-MeO; **LXIII**, R = *m*-MeO; R = **LXIV**, *p*-MeO; **LXV**, R = *o*-Cl; **LXVI**, R = *m*-Cl; **LXVII**, R = *p*-Cl; **LXVIII**, R = *o*-HOCO; **LXIX**, R = *m*-HOCO; **LXX**, R = *p*-HOCO.

signal ($W_{1/2}$ = 3.5 Hz). These data suggest *exo* orientation of 2-H and 3-H and hence *endo* orientation of the imide ring. No analogous broadening of the *syn*-7-H signal is observed in the ^{1}H NMR spectra of *exo*-imides **XXXI**–**XL**, which is consistent with the absence of *exo*-oriented protons in positions *2* and *3*. The 2-H and 3-H signals of *exo* isomers **XXXI**–**XL** are displaced upfield relative to the corresponding signals of *endo* isomers **XXI**–**XXX**, in keeping with published data [15, 16] on the chemical shifts of *endo*- and *exo*-protons in norbornane derivatives. In the ^{1}H NMR spectra of *trans*-diols **XXI**–**XL**, the 5-H and 6-H signals appear in a stronger field (δ 3.20–3.25 ppm against δ 6.10–6.55 ppm for initial norbornenes).

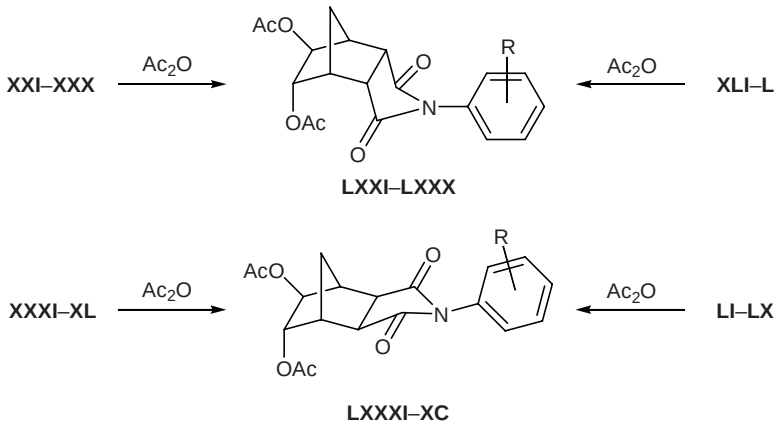
The mass spectra of *trans*-diols **XXI**–**XL** contain strong molecular ion peaks, fragment ion peaks corresponding to loss of one and two water molecules, as well as strong ion peaks with *m*/*z* 227, 198, 173, and 155. Their *cis* isomers showed in the mass spectra weak molecular ion peak, but a strong peak resulting from elimination of one water molecule from the molecular ion was present (*m*/*z* 255); no ion peaks with *m*/*z* 227 or 198 were observed. These findings confirm *trans* and *cis* configurations of the diols.

The presence of hydroxy groups in *trans*-5,6-dihydroxy derivatives **XXI**–**XL** was confirmed by their transformation into the corresponding diacetates **LXXI**–**XC** by treatment with excess acetic anhydride. Compounds **LXXI**–**XC** were also obtained by opening of the oxirane ring in **XLI**–**LX** under similar conditions (Scheme 4).

EXPERIMENTAL

The ^{1}H NMR spectra were recorded on a Tesla BS-487 spectrometer at 80 MHz using $CDCl_3$ as solvent and hexamethyldisiloxane as internal reference [17]. The IR spectra (400–3800 cm^{-1}) were measured on a UR-20 instrument from samples dispersed in mineral oil [12, 18]. The UV spectra were obtained on a Specord M-40 spectrophotometer. The purity of the products was checked by TLC on silica gel L (5–40 μm) [19]; detection under UV light.

Scheme 4.



LXXI, **LXXXI**, R = H; **LXXII**, **LXXXII**, R = *o*-MeO; **LXXIII**, **LXXXIII**, R = *m*-MeO; R = **LXXIV**, **LXXXIV**, *p*-MeO; **LXXV**, **LXXXV**, R = *o*-Cl; **LXXVI**, **LXXXVI**, R = *m*-Cl; **LXXVII**, **LXXXVII**, R = *p*-Cl; **LXXVIII**, **LXXXVIII**, R = *o*-HOCO; **LXXIX**, **LXXXIX**, R = *m*-HOCO; **LXXX**, **XC**, R = *p*-HOCO.

Table 1. Yields, melting points, R_f values, and elemental analyses of *N*-aryl-*trans*-5,6-dihydroxybicyclo[2.2.1]heptane-*endo*- and -*exo*-2,3-dicarboximides **XXI**–**XL**

Compound no.	Yield, %	mp, °C	R_f	Found, %				Formula	Calculated, %			
				C	H	Cl	N		C	H	Cl	N
XXI	91	199–200	0.69	66.31	5.05	–	6.05	$C_{15}H_{15}NO_4$	66.42	4.79	–	5.17
XXII	83	169–170	0.79	64.22	5.91	–	4.83	$C_{16}H_{17}NO_5$	63.66	5.61	–	4.60
XXIII	85	163–164	0.72	63.67	5.07	–	5.10	$C_{16}H_{17}NO_5$	63.66	5.61	–	4.60
XXIV	91	184–185	0.60	63.92	5.78	–	4.69	$C_{16}H_{17}NO_5$	63.66	5.61	–	4.60
XXV	93	201–202	0.75	59.01	4.61	12.01	4.72	$C_{15}H_{14}ClNO_4$	58.53	4.55	11.54	4.55
XXVI	95	227–228	0.76	59.42	4.47	11.17	4.92	$C_{15}H_{14}ClNO_4$	58.53	4.55	11.54	4.55
XXVII	90	202–203	0.70	59.13	5.11	12.03	4.52	$C_{15}H_{14}ClNO_4$	58.53	4.55	11.54	4.55
XXVIII	83	225–226	0.86	60.47	4.57	–	4.77	$C_{16}H_{15}NO_6$	60.56	4.73	–	4.41
XXIX	91	285–287	0.83	60.60	5.19	–	4.76	$C_{16}H_{15}NO_6$	60.56	4.73	–	4.41
XXX	94	260–261	0.81	60.79	4.82	–	4.53	$C_{16}H_{15}NO_6$	60.56	4.73	–	4.41
XXXI	93	202–203	0.60	66.00	4.86	–	4.61	$C_{15}H_{15}NO_4$	66.42	4.79	–	5.17
XXXII	92	177–178	0.51	62.71	4.79	–	3.99	$C_{16}H_{17}NO_5$	63.66	5.61	–	4.60
XXXIII	86	159–160	0.66	63.44	5.04	–	4.42	$C_{16}H_{17}NO_5$	63.66	5.61	–	4.60
XXXIV	94	206–207	0.59	63.41	5.09	–	4.32	$C_{16}H_{17}NO_5$	63.66	5.61	–	4.60
XXXV	97	180–181	0.73	57.98	4.43	11.50	4.22	$C_{15}H_{14}ClNO_4$	58.53	4.55	11.54	4.55
XXXVI	82	208–210	0.69	57.81	4.47	11.10	3.97	$C_{15}H_{14}ClNO_4$	58.53	4.55	11.54	4.55
XXXVII	91	160–161	0.68	57.43	4.50	11.41	4.51	$C_{15}H_{14}ClNO_4$	58.53	4.55	11.54	4.55
XXXVIII	81	220–222	0.87	60.93	4.81	–	4.72	$C_{16}H_{15}NO_6$	60.56	4.73	–	4.41
XXXIX	79	284–286	0.85	61.11	4.99	–	5.03	$C_{16}H_{15}NO_6$	60.56	4.73	–	4.41
XL	83	261–262	0.79	60.19	4.93	–	4.63	$C_{16}H_{15}NO_6$	60.56	4.73	–	4.41

N-Arylbicyclo[2.2.1]hept-5-ene-*endo*- and *exo*-2,3-dicarboximides **I**–**XX** were synthesized by the procedure described in [20].

***N*-Aryl-*trans*-5,6-dihydroxybicyclo[2.2.1]heptane-*endo*- and -*exo*-2,3-dicarboximides XXI–XL (*general procedure*).** *a*. One or two drops of concentrated sulfuric acid was added to a solution of 0.01 mol of *N*-aryl imide **I**–**XX** in 30 ml of acetic acid, and a mixture of 10 ml of 30% hydrogen peroxide and 10 ml of acetic acid was added under continuous stirring. The mixture was heated for 2 h at 70°C, 15 ml of water was added, and the mixture was heated for an additional 1 h. When the reaction was complete, the precipitate was filtered off, washed with water, and recrystallized from ethanol. The yields, melting points, R_f values, and elemental analyses of *trans*-diols **XXI**–**XL** are given in Table 1.

b. A mixture of 0.01 mol of *N*-aryl 5,6-*exo*-epoxybicyclo[2.2.1]heptane-*endo*- or -*exo*-2,3-dicarboximide **XLI**–**LX** and 30 ml of 5% sulfuric acid was heated for 4 h at 60°C. The precipitate was filtered off, washed with distilled water, and dried. Yield of *trans*-diols **XXI**–**XL** 78–90%.

Anhydrous peroxyacetic acid. A flask was charged with 72 g (1.2 mol) of acetic acid, 22.6 g of a 30% solution of hydrogen peroxide in dioxane, and 9.5 g (10 wt %) of KU-2 cation exchanger. The mixture was stirred for 3 h at 30°C until complete consumption of hydrogen peroxide and filtered from KU-2 through a Schott filter. The filtrate, 89.7 g, contained 58.8 g of acetic acid, 15.1 g of peroxyacetic acid, and 15.8 g of dioxane. The yield of peroxyacetic acid, calculated on the hydrogen peroxide taken, was 99.3%; concentration 16.8%.

***N*-Aryl-*exo*-5,6-epoxybicyclo[2.2.1]heptane-*endo*- and -*exo*-2,3-dicarboximides XLI–LX.** A solution of 0.01 mol of imide **I**–**XX** in 15 ml of dioxane was cooled to 8–10°C, and 10 ml of an anhydrous solution of peroxyacetic acid in dioxane was added, maintaining the temperature at 10°C. When peroxyacetic acid was consumed completely (3.5–4 h), the solvent and acetic acid were distilled off under reduced

Table 2. Yields, melting points, R_f values, and elemental analyses of *N*-aryl-*exo*-5,6-epoxybicyclo[2.2.1]heptane-*endo*- and -*exo*-2,3-dicarboximides **XLI**–**LX**

Compound no.	Yield, %	mp, °C	R_f	Found, %				Formula	Calculated, %			
				C	H	Cl	N		C	H	Cl	N
XLI	80	185–187	0.59	75.01	5.00	–	4.79	$C_{15}H_{13}NO_3$	74.90	5.09	–	5.49
XLII	87	160	0.60	67.17	5.16	–	4.80	$C_{16}H_{15}NO_4$	67.37	5.26	–	4.91
XLIII	90	154	0.60	67.07	5.30	–	5.19	$C_{16}H_{15}NO_4$	67.37	5.26	–	4.91
XLIV	87	164–165	0.54	66.81	5.19	–	5.10	$C_{16}H_{15}NO_4$	67.37	5.26	–	4.91
XLV	90	190–192	0.56	62.43	4.10	12.53	4.67	$C_{15}H_{12}ClNO_3$	62.18	4.14	12.26	4.84
XLVI	91	174–175	0.66	62.12	3.76	12.12	4.19	$C_{15}H_{12}ClNO_3$	62.18	4.14	12.26	4.84
XLVII	89	190–191	0.69	61.12	4.11	12.30	4.89	$C_{15}H_{12}ClNO_3$	62.18	4.14	12.26	4.84
XLVIII	87	207–208	0.825	63.62	4.17	–	5.02	$C_{16}H_{13}NO_5$	64.21	4.34	–	4.68
XLIX	90	241–242	0.78	64.60	3.75	–	4.92	$C_{16}H_{13}NO_5$	64.21	4.34	–	4.68
L	86	219–220	0.80	64.13	4.33	–	4.19	$C_{16}H_{13}NO_5$	64.21	4.34	–	4.68
LI	89	196–197	0.58	75.12	4.87	–	5.39	$C_{15}H_{13}NO_3$	74.90	5.09	–	5.49
LII	88	170–171	0.50	68.11	4.91	–	5.10	$C_{16}H_{15}NO_4$	67.37	5.26	–	4.91
LIII	93	154–155	0.62	68.01	5.35	–	5.19	$C_{16}H_{15}NO_4$	67.37	5.26	–	4.91
LIV	88	157–158	0.58	67.40	5.33	–	4.14	$C_{16}H_{15}NO_4$	67.37	5.26	–	4.91
LV	86	172–173	0.63	61.93	3.76	12.13	5.13	$C_{15}H_{12}ClNO_3$	62.18	4.14	12.26	4.84
LVI	90	190–191	0.67	62.08	4.21	11.78	5.06	$C_{15}H_{12}ClNO_3$	62.18	4.14	12.26	4.84
LVII	94	162–263	0.66	61.71	4.00	12.10	5.13	$C_{15}H_{12}ClNO_3$	62.18	4.14	12.26	4.84
LVIII	80	201–203	0.76	64.10	4.59	–	3.92	$C_{16}H_{13}NO_5$	64.21	4.34	–	4.68
LIX	83	235–236	0.80	64.92	4.73	–	4.53	$C_{16}H_{13}NO_5$	64.21	4.34	–	4.68
LX	87	241–243	0.67	63.93	3.89	–	4.99	$C_{16}H_{13}NO_5$	64.21	4.34	–	4.68

Table 3. Yields, melting points, R_f values, and elemental analyses of *N*-aryl-*cis*-5,6-dihydroxybicyclo[2.2.1]heptane-*endo*- and -*exo*-2,3-dicarboximides **LXI**–**LXX**

Compound no.	Yield, %	mp, °C	R_f	Found, %				Formula	Calculated, %			
				C	H	Cl	N		C	H	Cl	N
LXI	70	207	0.71	66.0	5.42	–	5.07	$C_{15}H_{15}NO_4$	65.93	5.49	–	5.13
LXII	60.4	239	0.73	63.14	5.25	–	4.21	$C_{16}H_{17}NO_5$	63.37	5.61	–	4.62
LXIII	67.5	252	0.70	63.50	5.37	–	4.12	$C_{16}H_{17}NO_5$	63.37	5.61	–	4.62
LXIV	62.8	255	0.68	63.16	5.39	–	4.20	$C_{16}H_{17}NO_5$	63.37	5.61	–	4.62
LXV	75.2	196	0.75	58.40	4.25	11.14	4.31	$C_{15}H_{14}ClNO_4$	58.53	4.55	11.54	4.55
LXVI	75.0	237	0.71	58.13	4.09	11.06	4.15	$C_{15}H_{14}ClNO_4$	58.53	4.55	11.54	4.55
LXVII	72.5	218	0.74	58.11	4.15	11.12	4.18	$C_{15}H_{14}ClNO_4$	58.53	4.55	11.54	4.55
LXVIII	60.6	236	0.68	60.12	4.51	–	4.37	$C_{16}H_{15}NO_6$	60.56	4.73	–	4.41
LXIX	64.5	255	0.70	68.18	4.29	–	4.27	$C_{16}H_{15}NO_6$	60.56	4.73	–	4.41
LXX	60.5	265	0.80	60.10	4.24	–	4.18	$C_{16}H_{15}NO_6$	60.56	4.73	–	4.41

pressure (water-jet pump), and the residue was recrystallized from anhydrous benzene. The yields, melting points, R_f values, and elemental analyses of compounds **XLI**–**LX** are given in Table 2.

***N*-Aryl-*cis*-5,6-dihydroxybicyclo[2.2.1]heptane-*endo*-2,3-dicarboximides LXI–LXX (*general procedure*).** A solution of 1.6 g of potassium permanganate in 250 ml of distilled water was added dropwise to a solution of 0.01 mol of imide **I**–**X** in 100 ml of acetone under vigorous stirring at room temperature. When potassium permanganate was consumed completely (the initial pink color disappeared), a dark brown solid separated (it turned colorless on treatment with dilute hydrochloric acid). The mixture was left to

Table 4. Yields, melting points, R_f values, and elemental analyses of *N*-aryl-*trans*-5,6-diacetoxybicyclo[2.2.1]heptane-*endo*- and -*exo*-2,3-dicarboximides **LXXI**–**XC**

Compound no.	Yield, %	mp, °C	R_f	Found, %				Formula	Calculated, %			
				C	H	Cl	N		C	H	Cl	N
LXXI	72	174–175	0.66	63.02	4.12	–	4.13	$C_{19}H_{19}NO_6$	63.86	5.32	–	3.92
LXXII	78	162–164	0.65	63.01	3.99	–	3.60	$C_{20}H_{21}NO_7$	62.02	5.69	–	3.62
LXXIII	80	159–160	0.61	62.16	5.59	–	4.21	$C_{20}H_{21}NO_7$	62.02	5.69	–	3.62
LXXIV	85	132–134	0.58	61.06	5.27	–	4.23	$C_{20}H_{21}NO_7$	62.02	5.69	–	3.62
LXXV	74	175–176	0.57	58.19	5.08	1.09	3.58	$C_{19}H_{18}ClNO_6$	58.23	4.59	9.06	3.57
LXXVI	70	146–148	0.65	57.98	5.05	9.72	3.52	$C_{19}H_{18}ClNO_6$	58.23	4.59	9.06	3.57
LXXVII	76	130–132	0.67	57.99	5.67	9.95	3.45	$C_{19}H_{18}ClNO_6$	58.23	4.59	9.06	3.57
LXXVIII	81	185–186	0.77	59.02	4.81	–	3.12	$C_{20}H_{19}NO_8$	59.99	4.74	–	3.49
LXXIX	71	194–195	0.71	59.66	4.65	–	3.37	$C_{20}H_{19}NO_8$	59.99	4.74	–	3.49
LXXX	73	186–188	0.74	60.11	4.95	–	3.14	$C_{20}H_{19}NO_8$	59.99	4.74	–	3.49
LXXXI	70	175–176	0.53	63.19	4.93	–	3.42	$C_{19}H_{19}NO_6$	63.86	5.32	–	3.90
LXXXII	69	163–164	0.48	61.75	5.33	–	3.47	$C_{20}H_{21}NO_7$	62.02	5.69	–	3.62
LXXXIII	70	140–141	0.60	61.90	4.97	–	3.59	$C_{20}H_{21}NO_7$	62.02	5.69	–	3.62
LXXXIV	71	163–164	0.51	62.10	5.81	–	3.17	$C_{20}H_{21}NO_7$	62.02	5.69	–	3.62
LXXXV	77	146–147	0.65	58.41	4.60	8.81	3.41	$C_{19}H_{18}ClNO_6$	58.23	5.69	9.06	3.57
LXXXVI	70	170–172	0.66	58.22	4.19	9.23	3.43	$C_{19}H_{18}ClNO_6$	58.23	4.59	9.06	3.57
LXXXVII	66	136–137	0.57	57.47	4.37	8.95	3.32	$C_{19}H_{18}ClNO_6$	58.23	4.59	9.06	3.57
LXXXVIII	72	171–173	0.74	59.60	4.63	–	3.31	$C_{20}H_{19}NO_8$	59.99	4.74	–	3.49
LXXXIX	73	210–211	0.71	60.01	4.68	–	3.47	$C_{20}H_{19}NO_8$	59.99	4.74	–	3.49
XC	69	200–202	0.64	59.57	5.08	–	3.57	$C_{20}H_{19}NO_8$	59.99	4.74	–	3.49

stand for 12 h, and the precipitate was filtered off and recrystallized from methanol. The yields, melting points, R_f values, and elemental analyses of *cis*-diols **LXI**–**LXX** are given in Table 3.

***N*-Aryl-*trans*-5,6-diacetoxybicyclo[2.2.1]heptane-*endo*- and -*exo*-2,3-dicarboximides LXXI–XC (*general procedure*).** A mixture of 0.1 mol of *trans*-5,6-diol **XXI**–**XL** or 5,6-epoxy derivative **XLI**–**LX**, KU-2 cation exchanger (H-form, 40% of initial reactant mixture), and 35 ml of acetic anhydride was heated for 6 h. When the reaction was complete, the mixture was filtered from KU-2, and crystals precipitated from the filtrate were were filtered off, washed with distilled water, and dried. The yields, melting points, R_f values, and elemental analyses of diacetates **LXXI**–**XC** are given in Table 4.

REFERENCES

1. Nazarov, I.N., Kucherov, V.F., and Bukharov, V.G., *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 1959, p. 328.
2. Yur'ev, Yu.K. and Zefirov, N.S., *Zh. Obshch. Khim.*, 1961, vol. 31, p. 840.
3. Kas'yan, L.I., Okovityi, S.I., Bombushkar', M.F., and Dryuk, V.G., *Russ. J. Org. Chem.*, 2000, vol. 36, p. 195; Kas'yan, L.I., Krishchik, O.V., Tarabara, I.N., Kas'yan, A.O., and Pal'chikov, V.A., *Russ. J. Org. Chem.*, 2006, vol. 42, 501.
4. Bagmanova, M.I., Bagmanov, B.T., and Umaeva, V.S., Abstracts of Papers, Konferentsiya *"Tonkii organicheskii sintez i kataliz"* (Conf. "Fine Organic Synthesis and Catalysis"), Baku, 1999, p. 47.
5. Malinovskii, M.S., *Khim. Geterotsikl. Soedin.*, 1974, p. 29.
6. Vereshchagin, A.N., Anastas'eva, A.P., and Arbuzov, B.A., *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1970, p. 995.
7. Salakhov, M.S. and Bagmanova, M.I., *Russ. J. Org. Chem.*, 2002, vol. 38, p. 244.
8. Bagmanov, B.T., Abstracts of Papers, *Konferentsiya molodykh uchenykh po probleme "Monomery i polimery"* (Conf. of Young Scientists on the Problem "Monomers and Polymers"), Sumgait, 1985, p. 5.
9. Meinwald, J., Nozaki, H., and Wiley, G.A, *J. Am. Chem. Soc.*, 1957, vol. 79, p. 5579.
10. *Organic Reactions*, Adams, R., Ed., New York: Wiley, 1954, vol. 8.

11. Sapunov, V.N. and Lebedev, N.N., *Zh. Obshch. Khim*., 1966, vol. 36, p. 273.
12. Kazitsyna, L.A. and Kupletskaya, N.B., *Primenenie UF-, IK-, YaMR- i mass-spektroskopii v organicheskoi khimii* (Application of UV, IR, NMR, and Mass Spectroscopy in Organic Chemistry), Moscow: Mosk. Gos. Univ., 1978.
13. Samitov, Yu.Yu., *Atlas spektrov yadernogo magnitnogo rezonansa prostranstvennykh izomerov* (Atlas of Nuclear Magnetic Resonance Spectra of Stereoisomers), Kazan: Kazan. Gos. Univ., 1978, vol. 1, p. 120.
14. Walborsky, H. and Loucrini, G., *J. Am. Chem. Soc*., 1954, vol. 76, p. 5396.
15. Kwart, H. and Loucrini, G., *J. Am. Chem. Soc*., 1954, vol. 76, p. 5400.
16. Henbest, H. and Nickels, B., *J. Chem. Soc.*, 1959, vol. 86, p. 221.
17. Bhacca, N.S. and Williams, D.H., *Applications of NMR Spectroscopy in Organic Chemistry. Illustrations from the Steroid Field*, San Francisco: Holden-Day, 1964. Translated under the title *Primenenie YaMR v organicheskoi khimii*, Moscow: Mir, 1966, pp. 151, 207.
18. Gordon, A.J. and Ford, R.A., *The Chemist's Companion*, New York: Wiley, 1972. Translated under the title *Sputnik khimika*, Moscow: Mir, 1976, p. 285.
19. Akhrem, A.A. and Kuznetsova, A.I., *Tonkosloinaya khromatografiya* (Thin-Layer Chromatography), Moscow: Nauka, 1965.
20. Salakhov, M.S., Musaeva, N.F., Suleimanov, S.N., and Bairamov, A.A., *Zh. Org. Khim*., 1979, vol. 15, p. 2326.