

Epoxidation of Bicyclo[2.2.1]hept-5-ene-2,3-*endo*- and Exodicarboxylic Acid N-Arylimides

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Abstract—Epoxidation of *endo*- and *exo*-bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic acid N-arylimides with a solution of peracetic acid in anhydrous dioxane affords 5,6-*exo*-epoxybicycloheptanedicarboxylic acid N-arylimides. The epoxidation reaction is not sensitive to the configuration of the imide fragment, to the character and position of the substituent in the aromatic ring. The reaction is determined only by oxidation conditions.

The epoxidation of unsaturated cyclic dicarboxylic acids is commonly performed as oxidation of the unsaturated bonds with peroxy acids [1]. The oxidation of the double bond in the anhydride of bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic acid with peracetic acid is known [2, 3] to occur exactly stereospecifically affording 5,6-*exo*-epoxyanhydride from the *exo*-anhydride, and *endo*- γ -lactone [4, 5] from the *endo*-anhydride.

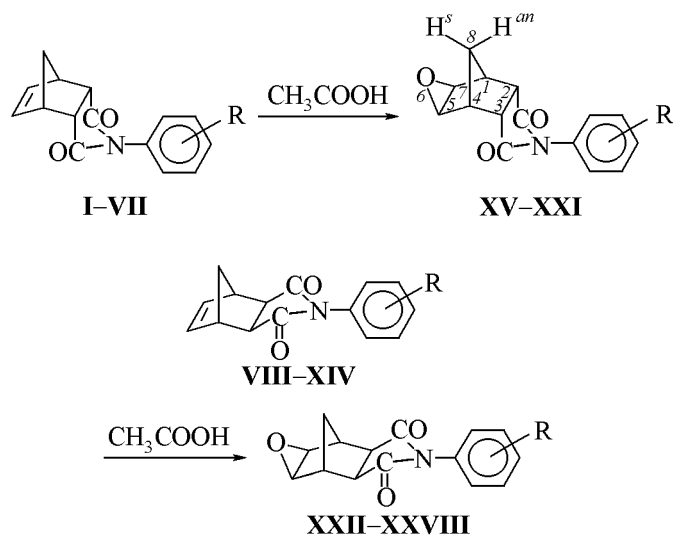
The present study concerns the behavior of the double bond in the *endo*- (I-VII) and *exo*- (VIII-XIV) isomers of bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic acid N-arylimides in the course of oxidation depending on the *endo* or *exo* configuration

of the imide ring, and on the character and position of the substituent in the aromatic ring. The oxidation of the double bond in N-arylimides I-XIV was carried out with a solution of peracetic acid in anhydrous dioxane. The solution of peracetic acid had been preliminary prepared from acetic acid and a 60% solution of hydrogen peroxide in dioxane.

We hoped to obtain epoxides XV-XXVIII stable under the reaction conditions for the presence of carbonyl groups in the imide ring should have stabilized the oxide cycle. The alteration in the negative inductive effect of the N-arylimide moiety was performed by means of electron-donor and electron-withdrawing groups introduces in *ortho*, *meta*, and *para* positions of the aromatic ring.

As a result of the investigation performed we revealed that irrespective of the character and position of substituents, and also of the imide ring configuration the oxidation of N-arylimides I-XIV with peracetic acid in anhydrous dioxane at room temperature occurred exactly stereospecifically and afforded highly heat-resistant epoxy compounds XV-XXVIII with the *exo*-configuration of the epoxy ring in nearly quantitative yield (95-98%). The oxygen attack occurred from the side of *endo*-methylene bridge notwithstanding *endo*- or *exo*-configuration of the imide fragment.

The presence of the epoxy ring in compounds XV-XXVIII is proved by IR spectra where is observed an absorption band in 851-860 cm^{-1} region characteristic of the epoxy ring, and absorption bands of C=O groups at 1704-1720 cm^{-1} [6, 7]. The *exo*-configuration of the epoxy ring in compounds XV-XXVIII follows from the ^1H NMR spectra where the

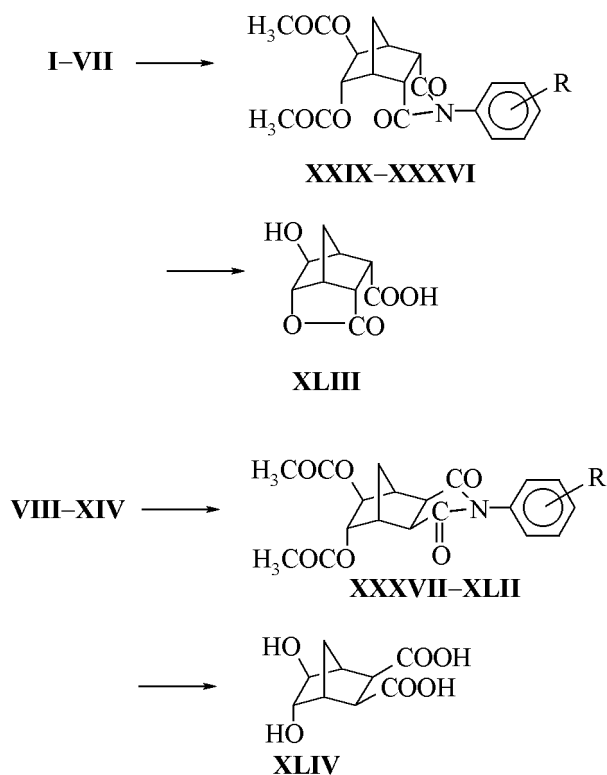


R = H (I, VIII, XV, XXII), *o*-, *m*-, *p*-OCH₃ (II-IV, IX-XI, XVI-XVIII, XXIII-XXV), *o*-, *m*-, *p*-COOH (V-VII, XII-XIV, XIX-XXI, XXVI-XXVIII).

signals of protons $H^{\delta s}$ and $H^{\delta an}$ appear as *AB*-quartet with the geminal coupling constant J 11 Hz demonstrating their nonequivalence. The assignment of signals belonging to the protons was done taking into account magnetically anisotropic effect of the oxirane ring resulting in the downfield shift of the $H^{\delta s}$ resonance [8].

The *exo*-configuration of imide ring in compounds **XXII–XXVIII** is proved by nonequivalence of H^5 and H^7 protons characteristic of all epoxy compounds in this series [9]. In the spectra of *endo*-isomers **XV–XXI** coupling constants of the *endo*-atoms H^5 and H^7 with the protons H^1 and H^4 (J 0–2 Hz) are smaller than in the spectra of *exo*-isomers **XXII–XXVIII** (J 2–4 Hz). The chemical shift of signal from $H^{\delta s}$ is 0.9 ppm for *exo*-isomers and 1.15 for *endo*-isomers [8].

It should be noted that epoxidation carried out under similar conditions but in the presence of sulfuric acid as catalyst instead of *exo*-epoxyimides **XV–XXVIII** arise *trans*-5,6-diacetoxy-*endo*- (**XXIX–XXXVI**) and *exo*- (**XXXVII–XLII**) dicarboxylic acid *N*-arylimides. Compounds **XV–XXVIII** on boiling with excess acetic acid in the presence of sulfuric acid also give rise to *trans*-5,6-diacetoxyimides **XXIX–XLII** that are colorless crystalline substances well soluble in acetone.



Hydrolysis of *endo*-isomers **XXIX–XXXVI** with 10% sulfuric acid (or 10% alkali) affords lactone **XLIII**, and hydrolysis of isomers **XXXVII–XLII** affords *trans*-5,6-dihydroxydicarboxylic acid **XLIV**. The *trans*-configuration of hydroxy groups in the hydroxyacid **XLIV** is confirmed by IR spectrum where appears only the absorption band of free hydroxy groups in the region 3465–3480 cm^{-1} . In the IR spectrum of lactone **XLIII** are present absorption bands at $\nu(\text{OH})$ 3420 and $\nu(\text{C}=\text{O})$ 1752 cm^{-1} [10].

EXPERIMENTAL

^1H NMR spectra were recorded on spectrometer Tesla BS-487 at operating frequency 80 MHz in CDCl_3 solutions, internal reference HMDS. IR spectra were measured on UR-20 instrument in 400–3800 cm^{-1} range from samples as mulls in mineral oil [6, 7].

The purity of compounds was checked by TLC, sorbent silica gel L 5/40 μ [11], development by UV irradiation.

Bicyclo[2.2.1]hept-5-ene-2,3-*endo*- and *exo*-dicarboxylic acid *N*-arylimides were prepared along procedure [12].

Peracetic acid. Hydrogen peroxide of 33% concentration was concentrated to 60% concentration by vacuum distillation, and the peroxide was extracted into ether. At 45–50°C the ether was distilled off with simultaneous addition of dioxane. Into the flask was charged 72 g (1.2 mol) of acetic acid, 22.6 g of 30% dioxane solution of hydrogen peroxide [6.8 g (0.2 mol) of H_2O_2], and 9.5 g (10% of overall weight) of cation-exchanger KU-2 in the H-form. The reaction was carried out at 30°C till complete consumption of hydrogen peroxide (within 3 h), then KU-2 was filtered off, and we obtained 89.7 g of solution containing 58.8 g of acetic acid, 15.2 g of peracetic acid, and 15.7 g of dioxane. The yield of peracetic acid with respect to the charged hydrogen peroxide was 99%. Concentration of peracetic acid in the mixture was 17%.

Oxidation of bicyclo[2.2.1]hept-5-ene-2,3-*endo*- and *exo*-dicarboxylic acid *N*-arylimides with peracetic acid. To a mixture of 0.01 mol of *N*-arylimide **I–XIV** and 15 ml of dioxane was added dropwise 10 ml of dioxane solution of peracetic acid maintaining the temperature of the reaction mixture on $\sim 10^\circ\text{C}$ level. On complete consumption of peracetic acid dioxane was distilled off from the reaction mixture, and the remaining crystalline product was recrystal-

Table 1. Yields, melting points, R_f values, elemental analyses, and molecular weight of epoxides (XV–XXVIII)

Compd. no.	Yield, %	mp, °C (solvent for crystallization)	R_f	Found, %			Formula	Calculated, %			M	
				C	H	N		C	H	N	found	calc.
XV	86	185 (ethanol)	0.59	75.01	4.87	5.29	C ₁₅ H ₁₃ NO ₃	74.90	4.87	5.49	253	255
XVI	90	168 (benzene)	0.61	67.17	5.16	4.80	C ₁₆ H ₁₅ NO ₄	67.37	5.26	4.91	284	286
XVII	87	175 (ethanol)	0.60	67.16	5.30	5.00	C ₁₆ H ₁₅ NO ₄	67.37	5.26	4.91	287	286
XVIII	87	155 (benzene)	0.54	66.81	5.19	5.02	C ₁₆ H ₁₅ NO ₄	67.37	5.26	4.91	285	286
XIX	88	208 (benzene)	0.82	63.62	4.17	4.62	C ₁₆ H ₁₃ NO ₅	64.21	4.34	4.68	293	295
XX	90	242 (ethanol)	0.78	64.60	3.75	4.52	C ₁₆ H ₁₃ NO ₅	64.21	4.34	4.68	296	295
XXI	86	220 (ethanol)	0.78	64.13	4.33	4.20	C ₁₆ H ₁₃ NO ₅	64.21	4.34	4.68	294	295
XXII	89	197 (ethanol)	0.58	74.82	4.97	5.39	C ₁₅ H ₁₅ NO ₃	74.90	5.09	5.49	254	255
XXIII	87	161 (benzene)	0.60	67.17	5.16	4.80	C ₁₆ H ₁₅ NO ₄	67.37	5.26	4.91	287	286
XXIV	90	175 (benzene)	0.62	67.07	5.28	5.00	C ₁₆ H ₁₅ NO ₄	67.37	5.26	4.91	286	286
XXV	89	158 (benzene)	0.58	67.40	5.25	4.38	C ₁₆ H ₁₅ NO ₄	67.37	5.26	4.91	285	286
XXVI	88	202 (benzene)	0.87	64.10	4.02	4.66	C ₁₆ H ₁₃ NO ₅	64.21	4.34	4.68	296	295
XXVII	90	235 (benzene)	0.71	63.88	4.02	4.33	C ₁₆ H ₁₃ NO ₅	64.21	4.34	4.68	293	295
XXVIII	90	241 (benzene)	0.67	63.92	3.89	4.06	C ₁₆ H ₁₃ NO ₅	64.21	4.34	4.68	292	295

Table 2. Yields, melting points, R_f values, elemental analyses, and molecular weight of *trans*-5,6-diacetoxycyclo[2.2.1]heptane-2,3-dicarboxylic acid N-arylimides **XXIX–XLII**

Compd. no.	Yield, %	mp, °C (solvent for crystallization)	R_f	Found, %			Formula	Calculated, %			M	
				C	H	N		C	H	N	found	calc.
XXIX	72	175 (benzene)	0.66	63.02	4.92	4.00	C ₁₉ H ₁₉ NO ₆	63.86	5.32	3.90	356.0	357.0
XXX	78	163 (benzene)	0.65	62.01	5.29	3.60	C ₂₀ H ₂₁ NO ₇	62.02	5.69	3.62	385.5	387.0
XXXI	80	160 (benzene)	0.61	62.06	5.59	4.00	C ₂₀ H ₂₁ NO ₇	62.02	5.69	3.62	388.0	387.0
XXXII	85	133 (benzene)	0.60	61.85	5.27	3.98	C ₂₀ H ₂₁ NO ₇	62.02	5.69	3.62	386.6	387.0
XXXIII	81	186 (benzene)	0.77	59.02	4.81	3.12	C ₂₀ H ₁₉ NO ₈	59.99	4.79	3.49	400.2	401.0
XXXIV	72	195 (benzene)	0.71	59.66	4.68	3.65	C ₂₀ H ₁₉ NO ₈	59.99	4.79	3.49	400.8	401.0
XXXV	73	187 (benzene)	0.74	59.66	4.65	3.12	C ₂₀ H ₁₉ NO ₈	59.99	4.79	3.49	401.2	401.0
XXXVI	70	176 (benzene)	0.73	63.29	4.98	3.42	C ₁₉ H ₁₉ NO ₆	63.86	5.32	3.90	355.8	357.0
XXXVII	69	164 (benzene)	0.77	61.75	5.33	3.47	C ₂₀ H ₂₁ NO ₇	62.02	5.69	3.62	387.5	387.0
XXXVIII	71	141 (benzene)	0.67	61.90	4.99	3.59	C ₂₀ H ₂₁ NO ₇	62.02	5.69	3.62	385.7	387.0
XXXIX	70	164 (benzene)	0.71	62.00	5.60	3.17	C ₂₀ H ₂₁ NO ₇	62.02	5.69	3.62	386.0	387.0
XL	72	172 (ethanol)	0.74	59.60	4.63	3.31	C ₂₀ H ₁₉ NO ₈	59.99	4.79	3.49	400.4	401.0
XLI	73	211 (ethanol)	0.78	59.68	4.68	3.48	C ₂₀ H ₁₉ NO ₈	59.99	4.79	3.49	400.6	401.0
XLII	70	201 (ethanol)	0.76	59.57	4.70	3.42	C ₂₀ H ₁₉ NO ₈	59.99	4.79	3.49	400.8	401.0

lized from benzene. The characteristics of epoxyimides obtained are given in Table 1.

***trans*-5,6-Diacetoxy endo- and exo-bicyclo[2.2.1] heptane-2,3-dicarboxylic acid N-arylimides (XXIX–XLII).** (a) To a solution of 0.01 mol of arylimides I–XIV in 10-fold excess of acetic acid with 2–3 ml of concn. sulfuric acid added thereto at room temperature and vigorous stirring was added drop-

wise within 1 h a mixture of 15 ml of 60% H₂O₂ and 15 ml of acetic acid. Due to heat evolution the reaction mixture warmed to 50–60°C, and after finishing the addition the reaction mixture was heated for 2 h to 70°C. On cooling the mixture precipitated crystals of compounds **XXIX–XLIII** that were filtered off and recrystallized from benzene. The characteristics of the reaction products are presented in Table 2.

(b) To a mixture of 0.01 mol of 5,6-exo-epoxy-bicyclo[2.2.1]heptane-2,3-dicarboxylic acid N-arylimide (**XXV-XXVIII**) was added 25 ml of acetic anhydride and 2–3 ml of concn. H_2SO_4 as catalyst. The mixture was heated for 6 h, then the reaction mixture was cooled, the precipitated crystalline reaction product **XXIX-XLII** was filtered off, washed with distilled water, and recrystallized from benzene.

Hydrolysis of 5,6-diacetoxycyclo[2.2.1]-heptane-2,3-dicarboxylic acid N-arylimides. (a) To 30 ml of 10% H_2SO_4 was added 0.01 mol of *endo*-isomer **XXIX-XXXVI** or *exo*-isomer **XXXVII-XLII**, and the mixture was left standing for 2 h. Then the mixture was heated to 35°C for 2 h, and on cooling precipitated a crystalline substance that was filtered off, washed with distilled water, and recrystallized from ethanol or benzene. From *endo*-isomers **XXIX-XXXVI** was obtained lactone **XLIII**, and from *exo*-isomers **XXXVII-XLII** was prepared hydroxyacid **XLIV**.

(b) A mixture of 0.01 mol of *endo*-isomer **XXIX-XXXVI** or *exo*-isomer **XXXVII-XLII** and 30 ml of 10% aqueous alkali was boiled for 6 h at 120–140°C and left for 12 h at room temperature. The separated crystalline product was filtered off, washed with distilled water, and recrystallized from ethanol or benzene. Yield of compound **XLIII** 77%, of compound **XLIV** 60%.

2-exo-Hydroxy-5-oxo-4-oxatricyclo[4.2.1.0^{3,7}]-nonane-9-carboxylic acid (XLIII). mp 110°C. R_f 0.25. Found, %: C 54.00; H 4.89. $C_9H_{10}O_5$. Calculated, %: C 54.54; H 5.05.

trans-5,6-Dihydroxybicyclo[2.2.1]heptane-2-exo-3-exo-dicarboxylic acid (XLIV). mp 145°C. R_f 0.44. Found, %: C 49.62; H 4.01. $C_9H_{12}O_6$. Calculated, %: C 50.00; H 4.44.

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