Transformations of anilides of 3-aryl-2,3-epoxypropionic acids when exposed to acidic agents*

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Anilides of 3-aryl-2,3-epoxypropionic acids on treatment with aqueous HBr gave 3-aryl-3-bromo-2-hydroxypropionic acid anilides and (in some cases) 2-bromo-3-hydroxy regioisomers. Cyclization of these products into 3-arylquinolin-2(1*H*)-ones was studied.

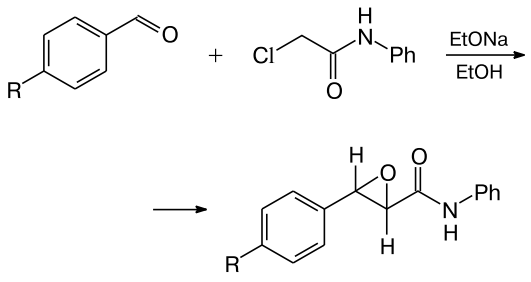
Key words: anilides of 3-aryl-2,3-epoxypropionic acids, anilides of 3-bromo-2-hydroxy-3-arylpropionic acids, quinolin-2(1*H*)-ones, X-ray diffraction analysis.

Synthetic procedures towards derivatives of 2,3-epoxypropionic acid are mostly limited by the Darzens reaction and its modifications.[1—8] 2,3-Epoxy-3-phenylpropionic acid anilide has been first synthesized in 1919;[7] however, the interest in this compound and other epoxypropionic acid amides has raised due only to the possibility to obtain enantiopure forms in the presence of chiral catalysts.[9—14] Recently,[15,16] transformations of 2,3-epoxypropionic acid anilides into quinolin-2-ones have been described. Synthesis of 4-aryl-3-hydroxyquinolin-2(1*H*)-ones from 3-aryl-2-cyanepoxypropionic acid *N*-methylanilides has been published.[15] We have synthesized 3-arylquinolin-2(1*H*)-ones starting from *N*-unsubstituted anilides of 3-aryl-2,3-epoxypropionic acid.[16] All these transformations were performed by treating the starting compounds with a solution of sulfuric acid in different solvents. In the present work, we studied a behavior of a series of 3-aryl-2,3-epoxypropionic acid anilides in the presence of hydrobromic acid and further transformations of thus obtained hydrobromination products upon treatment with sulfuric acid.

Results and Discussion

3-Aryl-2,3-epoxypropionic acid anilides (**1a—f**) were synthesized by the reaction of the corresponding benzaldehydes with α-chloroacetanilide in the presence of NaOEt in EtOH at room temperature. We used in this reaction benzaldehydes bearing a wide range of *para*-substituents exerting different electronic effects (Scheme 1). It was found that the synthesis of compounds **1a—e** can be accomplished using equimolar amounts of the reagents, but a large excess of the corresponding benzaldehyde is required for the synthesis of compound **1f** bearing a strong electron-donating substituent. We have shown earlier[16] that under these conditions *trans*-isomers of 3-aryl-2,3-epoxypropionic acid anilides are mainly formed. Therefore, in the reaction with hydrobromic acid *trans*-isomers of compounds **1a—d,f** were used.

Scheme 1



1a—f

R = H (**a**), Br (**b**), Me (**c**), NO_2 (**d**), CF_3 (**e**), OMe (**f**)

The reaction procedure involves the addition of 47% aqueous hydrobromic acid to the solutions of compounds **1a—e** in acetone and subsequent maintaining the reaction mixture at room temperature for 1 h. The reaction products either precipitate from the reaction mixture or were precipitated by adding water. The yields were nearly quantitative. The changes in the ^{1}H NMR spectra indi-

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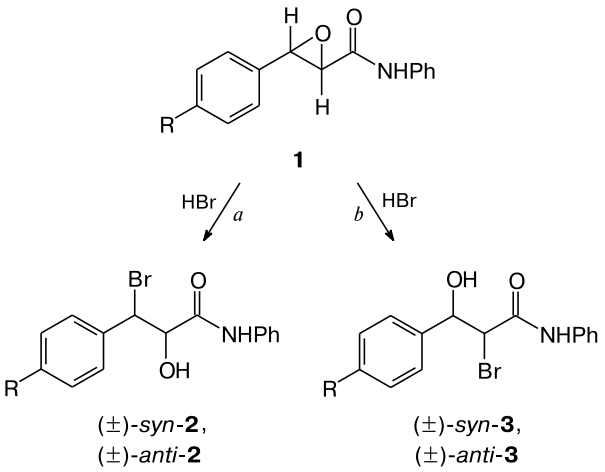
cate that the epoxide ring opening produces hydrobromination products.

The acid-catalyzed ring opening of epoxides may follow different directions; therefore, hydrobromination of 3-aryl-2,3-epoxypropionic acid anilides **1** can afford different isomeric products, namely, anilides of 3-bromo-2-hydroxy- (**2**) or 2-bromo-3-hydroxy-3-arylpropionic acids (**3**) (Scheme 2). In turn, each regioisomer can exist in two diastereomeric forms (*syn* and *anti*) consisting of one pair of enantiomers. It is impossible to make a conclusion about preferable direction of the epoxide ring opening due to the scarce published data. A detailed study has been undertaken only for hydrochlorination of methyl 2,3-epoxy-3-pnehylpropionate with hydrogen chloride in benzene to give methyl 3-chloro-2-hydroxy-3-phenylpropionate.[17]

Scheme 2



(±)-*syn*-**2**, (±)-*anti*-**2** (±)-*syn*-**3**, (±)-*anti*-**3**

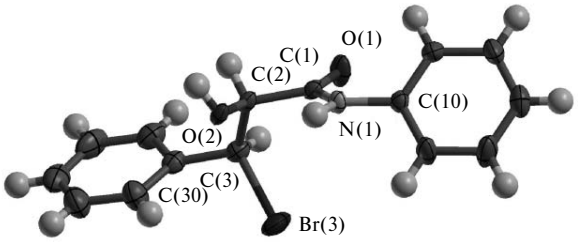


Fig. 1. Molecular structure of compound *anti*-**2a**. Nonhydrogen atoms are depicted at the 30% probability level; hydrogen atoms are shown as spheres of arbitrary radius.

^{1}H NMR chemical shifts of the C(2)H and C(3)H protons of *trans*-isomers of 3-aryl-2,3-epoxytropionic acid anilides (**1a—f**) and hydrobromination products are summarized in Table 1. From a comparison of these data with the data available for methyl 3-chloro-2-hydroxy-3-phenylpropionate,[17,18] the structures of anilides of 3-bromo-2-hydroxy-3-aryl propionic acid were supposedly ascribed to products **2a—c** (see Scheme 2, route *a*). Taking into account the same published data,[17,18] a diastereomers with the lower $^3J_{H,H}$ value were identified as *anti*. The *syn* : *anti* diastereomer ratios calculated from the integral intensities of the signals of the crude products are given in Table 1. We succeeded in resolving the individual *syn* and *anti* diastereomers of compounds **2a** and **2b**.

Single crystal X-ray diffraction structure of *anti*-**2a** (a single crystal was grown from a solution in chloroform) is shown on Fig. 1. According to X-ray diffraction analysis data, compound **2a** crystallizes as one independent molecule in the asymmetric part of the rhombic unit cell. The dihedral angle between the planes of two phenyl moieties is 36.6(2)°.

Table 1. ^{1}H NMR spectroscopy data (600 MHz, DMSO-d_6) of epoxides **1** and hydrobromination products

Compound	δ (*J*/Hz)			Product	R	*syn*/*anti*
	1	Product				
		syn	*anti*			
1a	3.78 (d, 1 H, *J* = 1.9); 4.20 (d, 1 H, *J* = 1.9)	4.66 (d, 1 H, *J* = 7.6); 5.36 (d, 1 H, *J* = 7.6)	4.42 (d, 1 H, *J* = 3.9); 5.57 (d, 1 H, *J* = 3.9)	**2a**	H	1 : 0.7
1b	3.76 (br.s, 1 H); 4.21 (br.s, 1 H)	4.62 (d, 1 H, *J* = 7.2); 5.35 (d, 1 H, *J* = 7.2)	4.38 (d, 1 H, *J* = 4.0); 5.53 (d, 1 H, *J* = 4.0)	**2b**	Br	1 : 0.5
1c	3.76 (d, 1 H, *J* = 1.7); 4.15 (d, 1 H, *J* = 1.7)	4.65 (d, 1 H, *J* = 7.5); 5.35 (d, 1 H, *J* = 7.5)	4.40 (d, 1 H, *J* = 4.1); 5.54 (d, 1 H, *J* = 4.1)	**2c**	Me	0.8 : 1
1d	3.84 (d, 1 H, *J* = 1.7); 4.42 (d, 1 H, *J* = 1.7)	4.58 (d, 1 H, *J* = 9.7); 5.12 (d, 1 H, *J* = 9.7)	4.70 (d, 1 H, *J* = 7.1); 5.52 (d, 1 H, *J* = 7.1)	**3d**	NO_2	0.05 : 1
1e	3.80 (d, 1 H, *J* = 1.29); 4.34 (d, 1 H, *J* = 1.28)	4.58 (d, 1 H, *J* = 9.8); 5.06 (d, 1 H, *J* = 9.8)	4.68 (d, 1 H, *J* = 7.3); 5.45 (d, 1 H, *J* = 7.3)	**3e**	CF_3	0.05 : 1
1f	3.80 (d, 1 H, *J* = 1.7); 4.13 (d, 1 H, *J* = 1.7)	4.17 (s, 2 H, H(3))[a] 6.47 (s, 1 H, H(3))[b]		**6**	OMe	1 : 0.3[c]

[a] Keto form. [b] Enol form. [b] A keto : enol ratio.

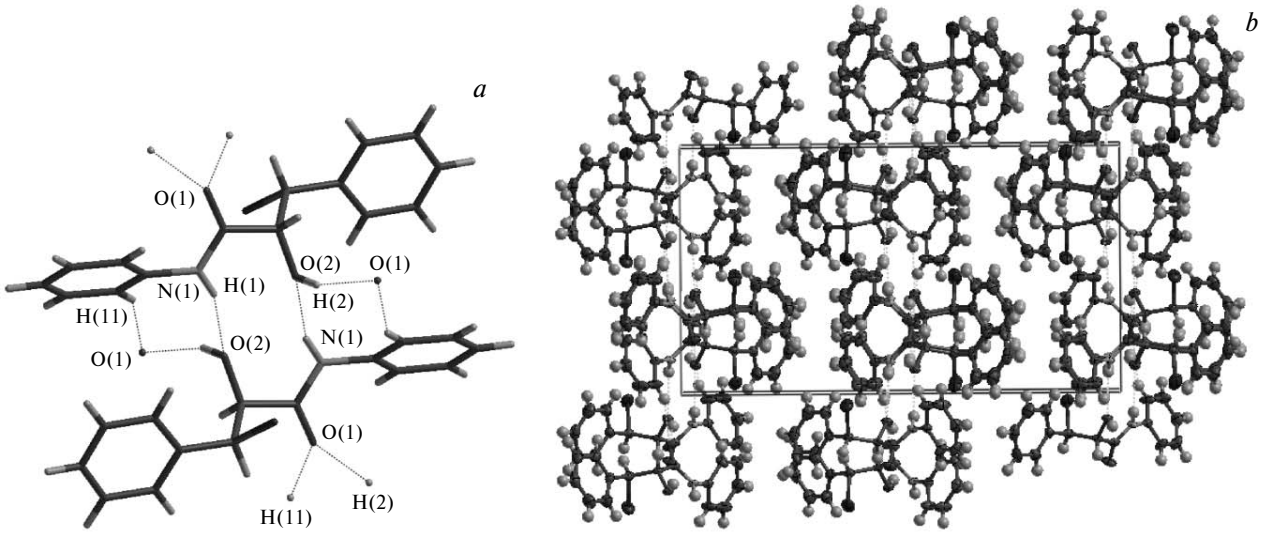


Fig. 2. *a*, H-Dimers in the crystal of compound formed by the NH...O hydrogen bonds (dashed lines). *b*, Fragment of crystal packing of molecules **2a**; view along the 0*b* axis.

Analysis of intermolecular interactions in the crystal indicates that the main supramolecular synthon is a symmetric H-dimer formed by a pair of the classical N—H...O hydrogen bonds (Fig. 2, *a*). The participation of the O(1) carbonyl oxygen in the bifurcated hydrogen bonds results in arrangement of the H-dimers in zigzag chains parallel to the *0ab* plane (Fig. 2, *b*). In general, the crystal structure of **2a** shows antiparallel packing of such zigzag motifs along the *0c* axes; the calculated molecular packing index is 66.3%. Note that only van der Waals forces virtually assemble the layers, since the parameters of π—π electron interactions between the aromatic moieties of the adjacent layers are close to the boundary values of the default criteria used in PLATON software for identification of such contacts.

Parameters of intermolecular and intramolecular contacts in compound **2a** found by X-ray diffraction analysis are summarized in Table 2.

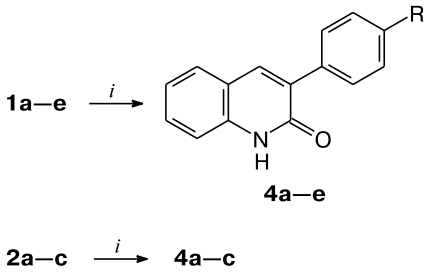
Compounds **2a**—**c** as either the diastereomeric mixtures or individual stereoisomers were involved in intramolecular cyclization[16] on treatment with sulfuric acid in dimethyl sulfate at 100 °C (Scheme 3). The reaction is accompanied by the aryl group migration to give 3-arylquinolin-2(1*H*)-ones **4a**—**c**. Compounds **4a**,**b**,**d** have been synthesized by us earlier from the corresponding 2,3-epoxy-3-arylpropionic acid anilides.[16] Compound **4c** was first synthesized in the present work starting from both 3-bromo-2-hydroxy-3-(4-methylphenyl)propionic acid anilide (**2c**) and 2,3-epoxy-3-(4-methylphenyl)propionic acid anilide (**1c**). Trifluoromethyl deriva-

Table 2. Parameters of intramolecular and intermolecular interaction in the crystals

D—H···A	D—H	H···A	D···A	DHA angle /deg	Symmetry code
	Å				
		Compound **2a**			
N(1)—H(1)...O(2)	0.86	2.26	2.668(4)	109	—
C(35)—H(35)...Br(3)	0.93	2.91	3.237(5)	102	—
N(1)—H(1)...O(2)	0.86	2.42	3.162(4)	145	$1-x, 1-y, -z$
O(2)—H(2)...O(1)	0.82	1.94	2.707(3)	156	$3/2-x, 1/2+y, z$
C(11)—H(11)...O(1)	0.93	2.43	3.278(5)	152	$-1/2+x, 1/2-y, -z$
		Compound **5**			
N(1)—H(1)...Br(2)	0.88(5)	2.46(4)	3.016(6)	122(4)	BMB
C(3)—H(3)...O(1)	0.93	2.32	2.737(8)	107	BMB
C(11)—H(11)...O(1)	0.93	2.24	2.836(9)	121	BMB
C(14)—H(14)...O(41A)	0.93	2.60	2.946(12)	103	BMB
C(35)—H(35)...Br(2)	0.93	2.57	3.278(8)	133	BMB
C(12)—H(12)...O(1)	0.93	2.44	3.309(9)	155	$2-x, 1-y, -z$

tive was synthesized only from epoxy anilide **1e** (see Scheme 3).

Scheme 3

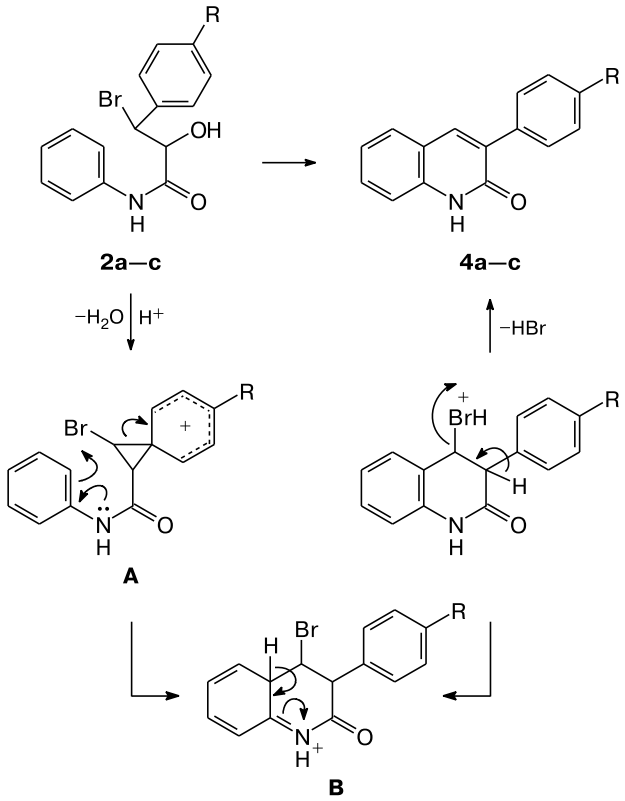


R = H (**a**), Br (**b**), Me (**c**), NO_2 (**d**), CF_3 (**e**)

i. H_2SO_4, Me_2SO_4, 100 °C.

A plausible mechanism for the formation of 3-arylquinolin-2(1*H*)-ones (**4a—c**) from 3-aryl-3-bromo-2-hydroxypropionic acid anilides **2a**,**c** is shown on Scheme 4. Migration of the aryl group can be explained by its anchimeric assistance[19] in stabilization of carbocation resulting from the hydroxy group cleavage. This leads to the intermediate structure **A**, which undergoes intramolecular Friedel—Crafts alkylation to give intermediate **B**. Stabilization of structure **B** occurs *via* the loss of HBr to produce the target product **4**.

Scheme 4



The data presented in Table 1 are not sufficient for the ascribing the structure of hydrobrominated compounds **3d**,**e** either to anilides of 3-aryl-2-bromo-3-hydroxypropionic acid (see Scheme 2, route *b*) containing predominantly the *anti* diastereomer or to a mixture of *syn*-diastereomers distinguished by positions of the Br atom and the OH group (see Scheme 2, routes *a* and *b*) with predominant isomer resulting from the route *a*. If the second possibility is implemented, the intramolecular cyclization catalyzed by sulfuric acid in dimethyl sulfate should result in 3-arylquinolin-2(1*H*)-ones similarly to compounds **2a—c**. According to the published data,[16] 2,3-epoxy-3-(4-nitrophenyl)propionic acid anilide (**1d**) produces 3-(4-nitrophenyl)quinolin-2(1*H*)-one (**4d**) in quantitative yield; in the present work, compound **1e** was transformed into 3-(4-trifluoromethylphenyl)quuinolin-2-one with high yield. However, the reactions of compounds **3d** and **3e** bearing the *para*-positioned strong electron-withdrawing substituents NO_2 and CF_3 afford hardly separable mixtures of the products. In ^{1}H NMR spectra of these mixtures, no signals characteristic of 3-arylquinolin-2(1*H*)-ones were found. These facts lead to the conclusion that the hydrobromination of compounds **1d**,**e** follows the route *b* to yield regioisomers **3d**,**e**.

According to X-ray diffraction study of a single crystal grown from a chloroform solution of the reaction mixture obtained by the reaction of **3d** with sulfuric acid in dimethyl sulfate, the product has structure of 2-bromo-3-(4-nitrophenyl)acrylic acid *N*-(4-methoxysulfonylphenyl)-amide (**5**) (Fig. 3).

In contrast to compound **2a**, the molecule of **5** has a planar geometry with strong conjugation, which is favored by the presence of two substituents on the aromatic ring participating in conjugation. At the same time, the methoxysulfonyl group is disordered over two positions with

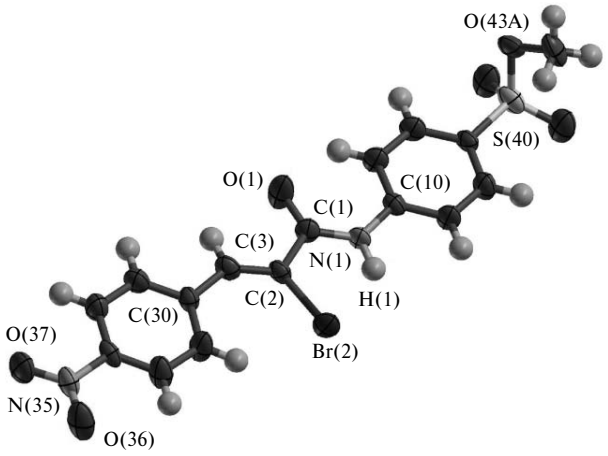


Fig. 3. Molecular structure of compound **5**. Nonhydrogen atoms are depicted at the 30% probability level; hydrogen atoms are shown as spheres of arbitrary radius. The methoxysulfonyl group is shown in the position with population parameter of 0.68.

Table 3. Parameters of π-interactions in the crystals of compound **5**

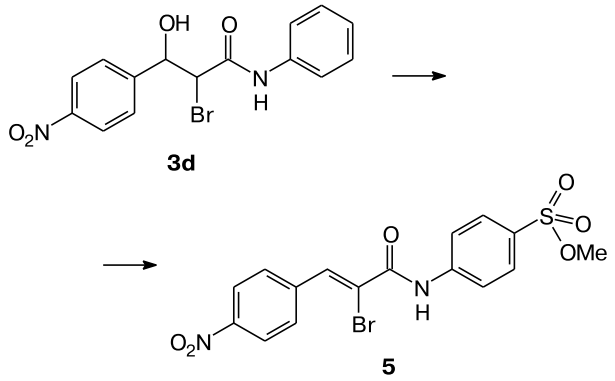
π-Contact	d^a/Å	φ^b/deg	Symmetry code
Cg(1)...Cg(2)[c]*	3.812(4)	4.8	$1-x, 1-y, -z$
Cg(2)...Cg(1)*	3.811(4)	4.8	$1-x, 1-y, -z$
Cg(1)...Cg(2)**	4.948(5)	4.8	$1-x, 2-y, -z$
Cg(2)...Cg(1)**	4.948(5)	4.8	$1-x, 2-y, -z$

[a] A distance between the centers of the cycles, Cg—Cg.
[b] Dihedral angle between the cycle planes.
[c] Cg1-cycle: C(10)—C(11)—C(12)—C(13)—C(14)—C(15), Cg2-cycle: C(30)—C(31)—C(32)—C(33)—C(34)—C(35). Symmetry codes for the interacting molecules: $(1-x, 1-y, -z)$(*) and $(1-x, 2-y, -z)$(**).

population parameters of 0.68 and 0.32. The planes of two aromatic substituents form a dihedral angle equal to 4.8(3)°. Despite the presence of amide function, it is not involved in intramolecular hydrogen bonding due apparently to the steric restrictions. In general, the intramolecular contacts are realized *via* the C—H...O hydrogen bonds and π-electron contacts (see Tables 2 and 3). These intramolecular interactions form a layered supramolecular structure parallel to the 0*ab* plane; the crystal packing is formed along the 0*c* axis (Fig. 4).

Apparently, product **5** is resulted from two reactions: acid-catalyzed dehydration to give the corresponding acrylic anilide and introduction of the methoxysulfonyl group into the phenyl ring (Scheme 5).

Scheme 5



Reagents and conditions: H^+, Me_2SO_4, 100 °C.

Under hydrobromination conditions, 2,3-epoxy-3-(4-methoxyphenyl)propionic acid anilide (**1f**) undergoes rearrangement accompanied by H-migration from C(2) to C(3) to give 3-(4-methoxyphenyl)-2-oxopropionic acid anilide (**6**) existing in the solutions in tautomeric equilibrium with the enol form (Scheme 6). A tautomeric ratio found by ^{1}H NMR spectroscopy and the chemical shifts of the C(3)H protons are given in Table 1. It is of note that

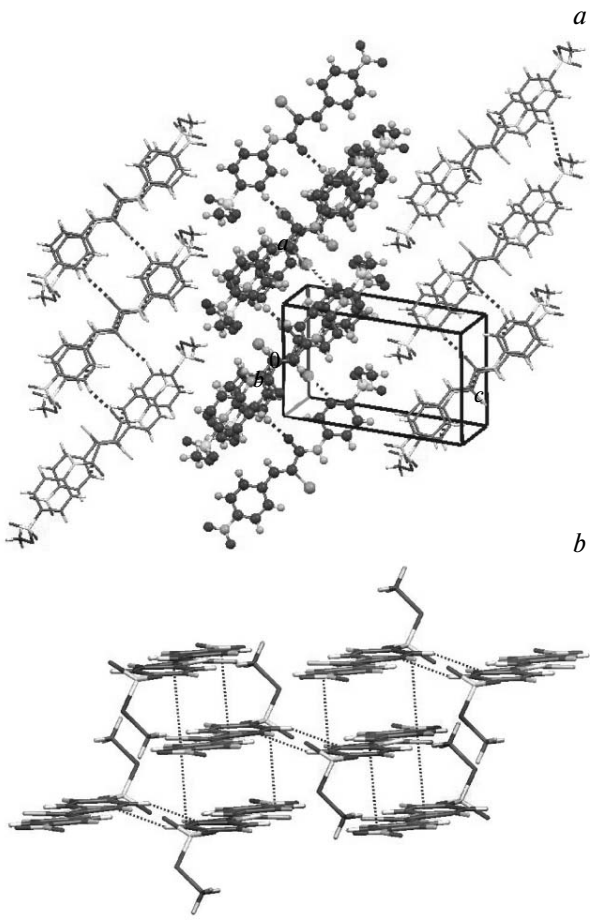
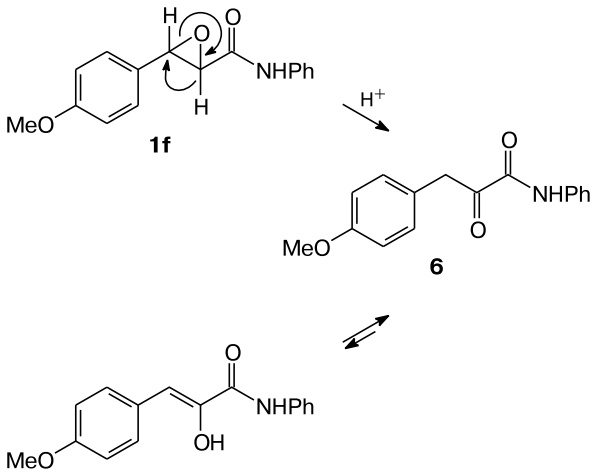


Fig. 4. *a*, A fragment of the layered supramolecular structure in crystal, the CH...O hydrogen bonds and π-contacts are shown by dashed lines. *b*, Mutual packing of the layers in crystal **5**. One of the layers is shown as ball-and-sticks models.

Scheme 6



the attempt to synthesize 3-(4-methoxyphenyl)quinolin-2-one from 2,3-epoxy-3-(4-methoxyphenyl)propionic acid anilide (**1f**) by treatment with sulfuric acid in dimethyl sulfate gives the same results.

In summary, the directions of the epoxide ring opening in the reactions of 3-aryl-2,3-epoxypropionic acid anilides with hydrobromic acid depend on electronic effects of the substituents on the aryl fragment. Treatment of 3-aryl-3-bromo-2-hydroxypropionic acid anilides with sulfuric acid in dimethyl sulfate at 100 °C produces 3-arylquinolin-2(1*H*)-ones, which being the analogs of natural alkaloids are of interest from the viewpoint of their biological activity.

Experimental

Melting points were measured on a Stuart SMP-10 apparatus. IR spectra were recorded with a Bruker Vector-22 instrument in Nujol. ^{1}H NMR spectra were run on a Bruker Avance-600 instrument in DMSO-d_6, the chemical shifts are given in the δ scale. High resolution MALDI mass spectrometry was performed with an UltraFlex III TOF/TOF spectrometer operating in a reflectron mode. 2,5-Dihydroxybenzoic acid and 4-nitroaniline were used as the matrixes. PEG-400 was used as an internal standard of mass calibration.

Single crystal X-ray diffraction analysis of compounds **2a** and **5** was carried out in the Laboratory of Diffraction Research Methods, the Federal Multiple-Access Center, A. E. Arbuzov Institute of Organic and Physical Chemistry of Kazan Research Center of the RAS. The diffraction experiments were performed with an automatized Bruker Smart Apex II CCD single crystal X-ray diffractometer (Mo-*K*α radiation, graphite monochromator, λ = 0.71073 Å, ω scan mode) at 23 °C. The data collection, data editing, and refinement of the unit cell parameters were performed with APEX2 program package.[20] A semi-empirical absorption corrections were applied using SADABS program.[21] The structures were solved by direct methods and refined by full matrix least-squares first isotropically, then anisotropically (for all non-hydrogen atoms) employing SHELXL software.[22] The hydrogen atoms of the hydroxy and amide groups of compounds **2a** and **5** were identified from difference electron density map and refined in isotropic approximation; all other hydrogen atoms were positioned using stoichiometric criteria and refined using a riding model. All computations were performed with WinGX program.[23] PLATON[24] and Mercury[25] programs were used for the analysis and visualization of the intramolecular interactions. Crystallographic parameters of compounds **2a** and **5**, details of the X-ray experiments, structure solution, and refinement parameters are summarized in Table 2. Crystallographic data for compounds **2a** and **5** were deposited with the Cambridge Crystallographic Data Centre (CCDC 1063781 and 1063782). These data can be obtained free of charge *via* Internet at www.ccdc.cam.ac.uk/data_request/cif.

3-Aryl-2,3-epoxypropionic acid anilides were synthesized by mixing chloroacetanilide and the corresponding benzaldehyde in equimolar amounts for compounds **1a**,**b**,**d**,**e** or using a 5-fold excess of benzaldehyde for compounds **1c**,**f**. The reactions were carried out in EtOH. Then ethanol solution of NaOEt in an amount equimolar to chloroacetic acid anilide was added followed by stirring the reaction mixture for 5 h. Similar procedure and physicochemical parameters of compounds **1a**,**b**,**d** have been published earlier.[16] Physicochemical properties of compounds **1c**,**e**,**f** are given below.

2,3-Epoxy-3-(4-methylphenyl)propionic acid anilide (1c). Here and hereafter the *trans* : *cis* isomeric ratios determined from ^{1}H NMR spectra of crude products are given. Other parameters and yields are given for *trans* isomers. *trans* : *cis* = 1 : 0.27. Yield 68%, m.p. 149—151 °C. Found (%): C, 75.82; H, 5.99; N, 5.58. $C_{16}H_{15}NO_2$. Calculated (%): C, 75.87; H, 5.97; N, 5.53. IR, ν/cm^{-1}: 744, 890, 1550, 1602, 1677, 3275. ^{1}H NMR, δ: 3.76, 4.15 (both d, 1 H each, H(2), H(3), J = 1.7 Hz); 7.09 (dd, 1 H, $H_{Ph}(4)$, $J_1 = J_2$ = 7.4 Hz); 7.22 (d, 2 H, $H_{Ar}(3)$ and $H_{Ar}(5)$, J = 7.8 Hz); 7.29 (d, 2 H, $H_{Ph}(2)$ and $H_{Ph}(6)$, J = 8.0 Hz); 7.34 (dd, 2 H, $H_{Ph}(3)$ and $H_{Ph}(5)$, J_1 = 7.9 Hz, J_2 = 7.5 Hz); 7.67 (d, 2 H, $H_{Ar}(2)$ and $H_{Ar}(6)$, J = 7.8 Hz); 10.23 (s, 1 H, NH). MS, *m*/*z*: 276.1016 $[M + Na]^+$. Calculated: $[M + Na]^+$ 276.0995.

2,3-Epoxy-3-(4-trifluoromethylphenyl)propionic acid anilide (1e), *trans* : *cis* = 1 : 0. Yield 99%, m.p. 187 °C. Found (%): C, 62.58; H, 3.90; F, 18,59; N, 4.52. $C_{16}H_{12}F_3NO_2$. Calculated (%): C, 62.54; H, 3.94, F, 18.55, N, 4.56. IR, ν/cm^{-1}: 1116, 1549, 1605, 1680, 3348. ^{1}H NMR, δ: 3.80, 4.34 (both d, 1 H each, H(2), H(3), J = 1.3 Hz); 7.10 (dd, 1 H, $H_{Ph}(4)$, $J_1 = J_2$ = 7.4 Hz); 7.34 (dd, 2 H, $H_{Ph}(3)$ and $H_{Ph}(5)$, J_1 = 7.6 Hz, J_2 = 8.1 Hz); 7.63 (d, 2 H, $H_{Ar}(2)$ and $H_{Ar}(6)$, J = 8.6 Hz); 7.65 (d, 2 H, $H_{Ar}(3)$ and $H_{Ar}(5)$, J = 8.7 Hz); 7.77 (d, 2 H, $H_{Ph}(2)$ and $H_{Ph}(6)$, J = 8.1 Hz); 10.32 (d, 1 H, NH). MS, *m*/*z*: 330.0718 $[M + Na]^+$. Calculated: $[M + Na]^+$ 330.0712.

2,3-Epoxy-3-(4-methoxyphenyl)propionic acid anilide (1f), *trans* : *cis* = 1 : 0. Yield 81%, m.p. 168—169 °C. Found (%): C, 71.39; H, 5.30; N, 5.25. $C_{16}H_{15}NO_3$. Calculated (%): C, 71.36; H, 5.61; N, 5.20. IR, ν/cm^{-1}: 1248, 1544, 1601, 1678, 3299. ^{1}H NMR, δ: 3.77 (s, 3 H, MeO); 3.80, 4.13 (both d, 1 H each, H(2), H(3), J = 1.7 Hz); 6.97 (d, 2 H, $H_{Ar}(3)$ and $H_{Ar}(5)$, J = 8.7 Hz); 7.09 (dd, 1 H, $H_{Ph}(4)$, $J_1 = J_2$ = 7.3 Hz); 7.33 (d, 2 H, $H_{Ar}(2)$ and $H_{Ar}(6)$, J = 8.7 Hz); 7.33 (dd, 2 H, $H_{Ph}(3)$ and $H_{Ph}(5)$, J_1 = 7.3 Hz, J_2 = 7.5 Hz); 7.67 (d, 2 H, $H_{Ph}(2)$ and $H_{Ph}(6)$, J = 7.6 Hz); 10.29 (c, 1 H, NH). MS, *m*/*z*: 402.0077 $[M + Cs]^+$. Calculated: $[M + Cs]^+$ 402.0101.

Reactions of compound 1a—f with HBr. To a solution of the corresponding 3-aryl-2,3-epoxypropionic acid anilide (1 mL) in acetone (10 mL), 47% aqueous hydrobromic acid (10 mL) was added. The reaction mixture was kept at room temperature for 1 h. After this period of time, products either precipitate from the reaction mixture or water was added to precipitate the target product. The precipitates were collected by filtration. According to ^{1}H NMR spectroscopy, the products were pure and contain no impurities. The diastereomeric ratios of products **2a**—**c**, **3d**,**e** and tautomeric ratio of **6** are given in Table 1. The yields were nearly quantitative.

***anti*-3-Bromo-2-hydroxy-3-phenylpropionic acid anilide (*anti*-2a).** The product precipitated from the reaction mixture within 20 min from the reaction onset, yield 0.08 g (25%), m.p. 143—145 °C. Found (%): C, 56.31; H, 4.48; Br, 25.02, N, 4.35. $C_{15}H_{14}BrNO_2$. Calculated (%): C, 56.27; H, 4.41; Br, 24.96; N, 4.37. IR, ν/cm^{-1}: 659, 1112, 1540, 1597, 1665, 3307. ^{1}H NMR, δ: 4.42, 5.57 (both d, 1 H each, H(2), H(3), J = 3.9 Hz); 7.07, 7.30, 7.36 (all dd, 1 H, 3 H, 2 H, $H_{Ph}(3)$, $H_{Ph}(4)$, $H_{Ph}(5)$, J = 7.2 Hz, J = 7.8 Hz, J = 7.2 Hz); 7.59, 7.65 (both d, 2 H each, $H_{Ph}(1)$, $H_{Ph}(6)$, J = 7.2 Hz, J = 7.8 Hz). MS, *m*/*z*: 451.9257 $[M + Cs]^+$. Calculated: $[M + Cs]^+$ 451.9281.

***syn*-3-Bromo-2-hydroxy-3-phenylpropionic acid anilide (*syn*-2a).** After filtration of *anti*-diastereomer, the filtrate was kept at room temperature for another 40 min, the precipitate containing a 1 : 1 mixture of *anti*- and *syn*-diastereomers was collected by filtration, yield 0.10 g (30%). The filtrate was diluted with water (30 mL), the precipitate of *syn*-**2a** was collected, yield 0.11 g (35%), m.p. 130—132 °C. Found (%): C, 56.29; H, 4.43; Br, 25.04,

N, 4.39. $C_{15}H_{14}BrNO_2$. Calculated (%): C, 56.27; H, 4.41; Br, 24.96; N, 4.37. IR, ν/cm^{-1}: 697, 767, 1101, 1543, 1602. 1671, 3354, 3474. ^{1}H NMR, δ: 4.66, 5.36 (both d, 1 H each, H(2), H(3), J = 7.6 Hz); 7.07, 7.30, 7.35 (all dd, 1 H, 3 H, 2 H, H_{Ph}(3), H_{Ph}(4), H_{Ph}(5), J = 7.3 Hz, J = 7.8 Hz, J = 7.3 Hz); 7.50, 7.59 (both d, 2 H each, H_{Ph}(2), H_{Ph}(6), J = 7.1 Hz, J = 7.7 Hz); 10.04 (s, 1 H, NH). MS, *m/z*: 359.9841 $[M + K]^+$. Calculated: $[M + K]^+$ 359.9820.

***syn*-3-Bromo-3-(4-bromophenyl)-2-hydroxypropionic acid anilide (*syn*-2b)** precipitated from the reaction mixture within 20 min from the reaction onset. Yield 0.18 g (45%), m.p. 147—148 °C. Found (%): C, 45.09; H, 3.33; Br, 40.07; N, 3.49. $C_{15}H_{13}Br_2NO_2$. Calculated (%): C, 45.14; H, 3.28; Br, 40.04; N, 3.51. IR, ν/cm^{-1}: 751, 1107, 1531, 1597, 1635, 3285. ^{1}H NMR, δ: 4.62, 5.35 (both d, 1 H each, H(2), H(3), J = 7.2 Hz); 7.07 (dd, 1 H, H_{Ph}(4), J_1 = J_2 = 7.5 Hz); 7.30 (dd, 2 H, H_{Ph}(3) and H_{Ph}(5), J_1 = 7.7 Hz, J_2 = 7.9 Hz); 7.45 (d, 2 H, H_{Ar}(2) and H_{Ar}(6), J = 8.5 Hz); 7.53 (d, 2 H, H_{Ar}(3) and H_{Ar}(5), J = 8.5 Hz); 7.56 (d, 2 H, H_{Ph}(2) and H_{Ph}(6), J = 7.9 Hz); 10.02 (s, 1 H, NH). ^{13}C NMR, δ: 56.6 (CHBr), 75.5 (CHOH), 120.4 (o-CH_{NHPh}), 122.0 (=CBr),124.3 (p-CH_{NHPh}), 129.1 (=CH), 131.3 (=CH), 131.6 (=CH), 138.6 (=C), 139.3 (=C), 169.8 (C=O). MS, *m/z*: 531.8357 $[M + Cs]^+$. Calculated: $[M + Cs]^+$ 531.8342.

***anti*-3-Bromo-3-(4-bromophenyl)-2-hydroxypropionic acid anilide (*anti*-2b).** After *syn*-diastereomer was collected, the reaction mixture was kept at room temperature for another 40 min to give a mixture of *anti*- and *syn*-diastereomers in a ratio of 0.5 : 1, yield 0.12 g (30%). This mixture was washed with $CHCl_3$ (3 mL). Removal of the volatiles from the filtrate afforded *anti*-**2b** in the yield of 0.07 g (18%), m.p. 168—170 °C. Found (%): C, 45.43; H, 3.41; Br, 40.96; N, 3.37. $C_{15}H_{13}Br_2NO_2$. Calculated (%): C, 45.14; H, 3.28; Br, 40.04; N, 3.51. IR, ν/cm^{-1}: 1112, 1544, 1603, 1659, 3339. ^{1}H NMR, δ: 4.38, 5.53 (both d, 1 H each, H(2), H(3), J = 4.0 Hz); 7.08 (dd, 1 H, H_{Ph}(4), J_1 = J_2 = 7.4 Hz); 7.29 (dd, 2 H, H_{Ph}(3) and H_{Ph}(5), J_1 = J_2 = 7.5 Hz); 7.51 (d, 4 H, H_{Ar}(2), H_{Ar}(3), H_{Ar}(5), and H_{Ar}(6), J = 3.8 Hz); 7.53 (dd, 2 H, H_{Ph}(2) and H_{Ph}(6), J_1 = J_2 = 7.5 Hz); 9.75 (s, 1 H, NH). ^{13}C NMR, δ: 56.6 (CHBr), 75.5 (CHOH), 120.4 (o-CH_{NHPh}), 122.0 (=CBr), 124.3 (p-CH_{NHPh}), 129.1 (=CH), 131.3 (=CH), 131.6 (=CH), 138.6 (=C), 139.3 (=C), 169.8 (C=O). MS, *m/z*: 531.8367 $[M + Cs]^+$. Calculated: $[M + Cs]^+$ 531.8342.

3-Bromo-2-hydroxy-3-(4-methylphenyl)propionic acid anilide (2c). The precipitate formed in the reaction mixture within 20 min after the reaction onset contained *syn*- and *anti*-diastereomers in a ratio of 0.8 : 1, yield 0.19 g (58%). Found (%): C, 57.59; H, 4.87; Br, 23.99; N, 4.02. $C_{16}H_{16}BrNO_2$. Calculated (%): C, 57.50; H, 4.83; Br, 23.91; N, 4.19. IR, ν/cm^{-1}: 753, 1053, 1549, 1601, 1656. ^{1}H NMR, δ: 2.28 (s, 3 H, Me); 4.40, 5.54 (both d, 1 H each, H_{anti}(2), H_{anti}(3), J = 4.1 Hz); 4.65, 5.35 (both d, 1 H each, H_{syn}(2), H_{syn}(3), J = 7.5 Hz); 6.90—7.70 (m, 9 H, C_6H_4, C_6H_5); 9.80 (s, 1 H, NH_{anti}); 10.03 (s, 1 H, NH_{syn}). The filtrate was kept at room temperature for another 40 min, the filtrate was collected by filtration, washed with chloroform to give 0.11 g (33%) of the substance, which was supposedly attributed to *anti*-2-bromo-3-hydroxy-3-(4-methylphenyl)propionic acid anilide, m.p. 175—176 °C. ^{1}H NMR, δ: 2.26 (s, 3 H, Me); 4.09, 4.94 (both d, 1 H each, H(2), H(3), J = 2.8 Hz); 7.07 (dd, 1 H, H_{Ph}(4), J_1 = J_2 = 7.8 Hz); 7.12 (d, 2 H, H_{Ar}(3) and H_{Ar}(5), J = 7.9 Hz); 7.29 (d, 2 H, H_{Ph}(2) and H_{Ph}(6), J = 8.0 Hz); 7.31 (dd, 2 H, H_{Ph}(3) and H_{Ph}(5), J_1 = 7.8, J_2 = 8.0 Hz); 7.64 (d, 2 H, H_{Ar}(2) and H_{Ar}(6), J = 7.9 Hz); 9.52 (s, 1 H, NH). MS, *m/z*: 465.9433 $[M + Cs]^+$. Calculated: $[M + Cs]^+$ 465.9413.

***anti*-2-Bromo-3-hydroxy-3-(4-nitrophenyl)propionic acid anilide (3d)** precipitated from the reaction mixture within 40 min after the reaction onset, yield 0.30 g (83%), m.p. 161 °C. Found (%): C, 49.38; H, 3.31; Br, 21.53; N, 7.38. $C_{15}H_{13}BrN_2O_4$. Calculated (%): C, 49.33; H, 3.59; Br, 21.88; N, 7.67. IR, ν/cm^{-1}: 875, 1115, 1350, 1517, 1599, 1663, 3321. ^{1}H NMR, δ: 4.70, 5.52 (both d, 1 H each, H(2), H(3), J = 7.1 Hz); 7.08 (dd, 1 H, H(4), Ph, J_1 = J_2 = 7.3 Hz); 7.31 (dd, 2 H, H_{Ph}(3) and H_{Ph}(5), J_1 = 7.5 Hz, J_2 = 7.9 Hz); 7.60 (d, 2 H, H_{Ph}(2) and H_{Ph}(6), J = 7.8 Hz); 7.79 (d, 2 H, H_{Ar}(2) and H_{Ar}(6), J = 8.6 Hz); 8.22 (d, 2 H, H_{Ar}(3) and H_{Ar}(5)); 10.07 (s, 1 H, NH). ^{13}C NMR, δ: 52.3 (CHBr), 75.8 (CHOH), 120.2 (o-CH_{NHPh}), 123.8 (=CH), 124.3 (p-CH_{NHPh}), 129.2 (=CH), 130.8 (=CH), 138.8 (=C), 146.3 (=C), 147.7 (=C), 169.3 (C=O). The filtrate was diluted with water (30 mL), filtration afforded a mixture of *anti*- and *syn*-diastereomers in a ratio of 2 : 1, yield 0.05 g (14%). MS, *m/z*: 365.0118 $[M + H]^+$. Calculated: $[M + H]^+$ 365.0131.

***anti*-2-Bromo-3-hydroxy-3-(3-trifluoromethylphenyl)propionic acid anilide (*anti*-3e)** precipitated from the reaction mixture within 40 min from the reaction onset, yield 0.32 g (86%), m.p. 168 °C. Found (%): C, 49.40; H, 3.24; Br, 20.93; F, 14,57; N, 3.32. $C_{16}H_{13}BrF_3NO_2$. Calculated (%): C, 49.51; H, 3.38; Br, 20,58; F, 14.68; N, 3.61. IR, ν/cm^{-1}: 749, 1113, 1127, 1329, 1530, 1599, 1636, 3293. ^{1}H NMR, δ: 4.68, 5.45 (both d, 1 H each, H(2), H(3), both J = 7.3 Hz); 7.08 (dd, 1 H, H_{Ph}(4), J_1 = J_2 = = 7.4 Hz); 7.31 (dd, 2 H, H_{Ph}(3) and H_{Ph}(5), J_1 = 7.6 Hz, J_2 = 7.7 Hz); 7.59 (d, 2 H, H_{Ph}(2) and H_{Ph}(6), J = 7.7 Hz); 7.73 (br.s, 4 H, H_{Ar}(2), H_{Ar}(3), H_{Ar}(5) and H_{Ar}(6)); 10.07 (s, 1 H, NH). The filtrate was diluted with water (30 mL), the precipitate containing a mixture of *anti*- and *syn*-diastereomers in a ratio of 2 : 1 was collected by filtration, yield 0.05 g (13%). MS, *m/z*: 519.9149 $[M + Cs]^+$. Calculated: $[M + Cs]^+$ 519.9131.

3-Arylquinolin-2(1*H*)-ones (4a—c) were synthesized by heating the corresponding 3-aryl-3-bromo-2-hydroxypropionic acid anilide (**2a—c**) (1 mmol) in a mixture of dimethyl sulfate (4 mL) and concentrated H_2SO_4 (1 mL) at 100 °C for 5 h. The reaction mixture was poured into water, the precipitate formed was collected by filtration. Compounds **4a**,**b** were synthesized earlier[21] from the corresponding 3-aryl-2,3-epoxypropionic acid anilides (**1a**,**b**); therefore, herein only the yields of **4a**,**b** are given. Compound **4c** was first synthesized and fully characterized in the present work.

3-Phenylquinolin-2(1*H*)-one (4a) was synthesized from *syn*-**2a**, *anti*-**2a**, and a mixture of diastereomers *syn*-**2a** and *anti*-**2a** (1 : 1) in the yields of 78, 82, and 80%, respectively.

3-(4-Bromophenyl)quinolin-2(1*H*)-one (4b) was synthesized from *syn*-**2b** in 89% yield.

3-(4-Methylphenyl)quinolin-2(1*H*)-one (4c) was synthesized following the known procedure[16] from a mixture of *syn*-**2c** and *anti*-**2c** (0.8 : 1) in 83% yield and from compound **1c** in 70% yield, m.p. 209—211 °C. Found (%): C, 81.72; H, 5.73; N, 6.02. $C_{16}H_{13}NO$. Calculated (%): C, 81.67; H, 5.58, N, 5.95. IR, ν/cm^{-1}: 1658. ^{1}H NMR, δ: 2.34 (s, 3 H, Me); 7.18, 7.48 (both dd, 1 H each, H(6), H(7) in the quinoline fragment (Q), J_1 = 7.4 Hz, J_2 = 7.6 Hz, J_3 = 7.4 Hz, J_4 = 8.1 Hz); 7.23 (d, 2 H, H_{Ar}(3) and H_{Ar}(5), J = 8.1 Hz); 7.34, 7.71 (both d, 1 H each, H_Q(5), H_Q(8), J = 8.1 Hz, J = 7.6 Hz); 7.66 (d, 2 H, H_{Ar}(2) and H_{Ar}(6), J = 8.0 Hz); 8.04 (s, 1 H, =CH); 11.88 (br.s, 1 H, NH). MS, *m/z*: 368.0075 $[M + Cs]^+$. Calculated: $[M + Cs]^+$ 368.0046.

3-(4-Nitrophenyl)quinolin-2(1*H*)-one (4d) was synthesized similarly to compound **4e** (see below) following the known procedure.[16]

3-(4-Trifluoromethylphenyl)quinolin-2(1*H*)-one (4e) was synthesized under previously described conditions[16] by treatment of 2,3-epoxy-3-(4-trifluoromethylphenyl)propionic acid anilide (**1e**) (0.51 g, 1.67) with a solution of H_2SO_4 in dimethyl sulfate. Yield 0.08 g (89%), m.p. 249—250 °C. Found (%): C, 66.32; H, 3.52; F, 19.92; N, 4.89. $C_{16}H_{10}F_3NO$. Calculated (%): C, 66.44; H, 3.48; F, 19.70; N, 4.84. IR, ν/cm^{-1}: 1664. ^{1}H NMR, δ: 7.22, 7.54 (both dd, 1 H each, $H_Q(6)$, $H_Q(7)$, $J_1 = 7.4$ Hz, $J_2 = 7.6$ Hz, $J_3 = 7.4$ Hz, $J_4 = 8.2$ Hz); 7.36, 7.51 (both d, 1 H each, $H_Q(5)$, $H_Q(8)$, $J = 8.2$ Hz, $J = 7.6$ Hz); 7.28, 7.99 (both d, 2 H each, H(2), H(6) and H(3), $H_{Ar}(5)$, $J = 8.2$ Hz); 8.22 (s, =CH); 12.03 (br.s, NH).

Reactions of 3-aryl-2-bromo-3-hydroxypropionic acid anilides 3d,e with H_2SO_4 carried out under previously described conditions[16] led to hardly separable mixtures, whose ^{1}H NMR spectra did not contain signals characteristic of 3-arylquinolin-2(1*H*)-ones. In the case of **3e**, we succeeded in isolation of 2-bromo-3-(4-nitrophenyl)acrylic acid *N*-(4-methoxysulfonylphenyl)amide (**5**) by recrystallization from chloroform.

2-Bromo-3-(4-nitrophenyl)acrylic acid *N*-(4-methoxysulfonylphenyl)amide (5). Yield 17%, m.p. 143—145 °C. Found (%): C, 43.63; H, 2.72; Br, 17.58; N, 6.18; S, 7.11. $C_{16}H_{13}BrN_2O_6S$. Calculated (%): C, 43.55; H, 2.97; Br, 18.11; N, 6.35; S, 7.27. IR, ν/cm^{-1}: 878, 1140, 1180, 1575, 1658, 1703, 3315. ^{1}H NMR, δ: 3.83 (s, 3 H, OMe); signals of the 4 $MeOC_6H_4SO_2$ and 4-$O_2NC_6H_4$ moieties: 7.78 (d, 2 H, H(3), H(5), $J = 8.7$ Hz), 7.85 (d, 2 H, H(3), H(5), $J = 8.5$ Hz), 7.92 (d, 2 H, H(2), H(6), $J = 8.5$ Hz), 8.22 (d, 2 H, H(2), H(6), $J = 8.7$ Hz); 10.51 (br.s, 1 H, NH).

3-(4-Methoxyphenyl)-2-oxopropanoic acid anilide (6). Method ***A***. Compound **6** was synthesized as above by treatment of anilide **1f** with hydrobromic acid. Yield 0.26 g (97%).

Method ***B***. To anilide **1f** (0.45 g, 1.67 mmol), a mixture of dimethyl sulfate (4 mL) and concentrated H_2SO_4 (1 mL) was added. The reaction mixture was heated at 100 °C for 5 h, then cooled to room temperature and poured into water. The precipitate formed was collected by filtration and washed with acetone. The removal of the volatiles from the filtrate afforded compound **6** in the yield 0.32 g (72%). M.p. 124 °C. Found (%): C, 71.42; H, 5.58; N, 5.50. $C_{16}H_{15}NO_3$. Calculated (%): C, 71.36; H, 5.61; N, 5.20. IR, ν/cm^{-1}: 757, 1256, 1519, 1536, 1604, 1668, 1724, 3335. ^{1}H NMR, δ, keto form: 3.72 (s, 3 H, OMe); 4.17 (s, 2 H, CH_2); 6.88 (d, 2 H, $H_{Ar}(3)$ and $H_{Ar}(5)$, $J = 8.3$ Hz); 7.12 (dd, 1 H, $H_{Ph}(4)$, $J_1 = J_2 = 7.4$ Hz); 7.17 (d, 2 H, $H_{Ar}(2)$ and $H_{Ar}(6)$, $J = 8.3$ Hz); 7.34 (dd, 2 H, $H_{Ph}(3)$ and $H_{Ph}(5)$, $J_1 = J_2 = 7.8$ Hz); 7.77 (d, 2 H, $H_{Ph}(2)$ and $H_{Ph}(6)$, $J = 7.9$ Hz); 10.45 (s, 1 H, NH); enol form: 3.76 (s, 3 H, OMe); 6.47 (s, 1 H, CH=); 6.94 (d, 2 H, $H_{Ar}(3)$ and $H_{Ar}(5)$, $J = 8.5$ Hz); 7.09 (dd, 1 H, $H_{Ph}(4)$, $J_1 = J_2 = 7.8$ Hz); 7.15 (d, 2 H, H(2), H(6), $J = 8.5$); 7.34 (dd, 2 H, $H_{Ph}(3)$ and $H_{Ph}(5)$, $J_1 = J_2 = 7.8$ Hz); 7.77 (d, 2 H, $H_{Ph}(2)$ and $H_{Ph}(6)$, $J = 7.2$ Hz); 10.02 (s, 1 H, NH); the ratio of keto : enol = 1 : 0.3. MS, *m/z*: 270.1146 $[M + H]^+$. Calculated: $[M + H]^+$ 270.1125.

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