Acid catalyzed rearrangements of aryl 3-(2-nitroaryl)oxiran-2-yl ketones*

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Studies of chemical behavior of aryl 3-(2-nitrophenyl)oxiran-3-yl ketones in acidic medium revealed the possible occurrence of two competitive rearrangements leading to 2-(2-oxo-2-arylacetamido)benzoic acids and 3-hydroxyquinolin-4(1*H*)-ones.

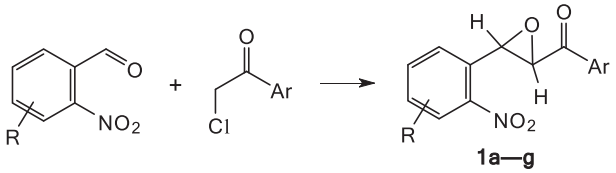
Key words: oxiranes, aryl 3-(2-nitroaryl)oxiran-3-yl ketones, rearrangements, anthranilic acid derivatives, 2-(2-oxo-2-arylacetamido)benzoic acids, 3-hydroxyquinolin-4-ones.

Oxirane derivatives are of great importance for organic synthesis.[1—8] Despite the large number of publications devoted to the chemistry of oxirane derivatives, the publications describing their unexpected transformations still appear.[9—14]

Earlier,[11,12] we have performed detailed studies on the chemical behavior of 3-aryl-2,3-epoxypropionic acid anilides in acidic medium. It has been found[11] that sulfuric acid-mediated tandem transformation[7] of these anilides *via* the Meinwald-type rearrangement with a 1,2-aryl shift and subsequent intramolecular Friedel—Crafts cyclization provided a quinolinone scaffold. However, if the aryl substituent at the oxirane ring has the *ortho*-positioned nitro group, the dramatically different result has been obtained. The brief reflux of the starting material quantitatively afforded N^1-(2-carboxyphenyl)-N^2-(aryl)oxalamides that can be considered as the derivatives of both oxalic and anthranilic acids.[12] This unique atom economic transformation involved the Meinwald rearrangement with the hydrogen shift, intramolecular redox reaction, the C—C bond cleavage, and the C—N bond formation.[7,12] Under the experimental conditions, some aryl 3-(2-nitroaryl)oxiran-2-yl ketones **1** underwent similar transformations to give the corresponding anthranilic acid derivatives. However, compounds **1** gave the products in the yields lower than those achieved from 3-(2-nitrophenyl)-2,3-epoxypropionic acid anilides.

In the present work, we studied in detail the chemical behavior of various aryl 3-(2-nitroaryl)oxiran-2-yl ketones **1** that were synthesized by the Darzens condensation[15] (Scheme 1) in acetic acid in the presence of sulfuric acid.

Scheme 1



1a—g

1	R	Ar
a	H	Ph
b	H	4-MeC_6H_4
c	H	4-$MeOC_6H_4$
d	H	4-ClC_6H_4
e	H	Naphthalen-1-yl
f	5-Cl	4-$MeOC_6H_4$
g	4-NO_2	4-ClC_6H_4

Reagents and conditions: MeONa, MeOH, 15 °C, 15 min.

With the aim to increase the yields of the anthranilic derivatives, we lowered the reaction temperature, and the reaction mixtures were heated to dissolve compounds **1** but not refluxed. Compounds **1a—c** in the amounts of 1.5 mmol dissolve in a mixture of AcOH (4 mL) and H_2SO_4 (0.2 mL) at water bath temperatures of 28, 40, and 65 °C, respectively; while, the reaction mixture temperatures reach 45, 50, and 73 °C. This is indicative of the exothermic reactions and the reactions were completed under stirring within 10 min. To dissolve compounds **1d—g** under similar conditions, the external heating temperature of 85 °C is needed, and in the case of compounds **1e**,**g** longer stirring time (30 min) is required to complete the reaction. From the reaction mixtures obtained using compounds **1d—g** as the starting materials, anthranilic acid derivatives **2d—g** (Scheme 2) were isolated in the yields of 78, 72, 84, and 77%, respectively. The ^{1}H NMR spec-

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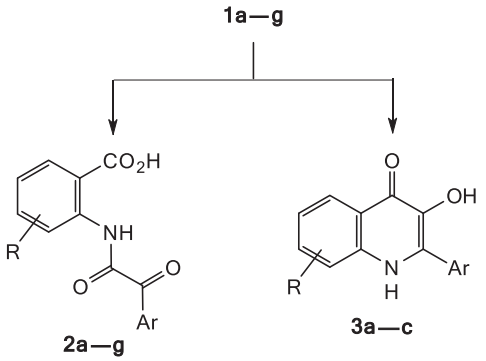
Scheme 2



Reagents and conditions: AcOH, H_2SO_4, 45—90 °C, stirring, 10—30 min.

tra of the crude products isolated by an aqueous workup of the reaction mixtures obtained by heating compounds **1a—c** in AcOH—H_2SO_4 (thick dark-brown oils in the case of **1a**,**b** and brownish solid in the case of **1c**) show the signals for the second product at δ 11.70, 11.80, and 11.78 along with the NH proton signals of products **2a—c** at δ 12.38, 12.35, and 12.34 (the integral intensity ratios of these signals are 1 : 1, 1 : 0.6, 1 : 0.5, respectively) (Table 1). From the reaction mixtures obtained by heating compounds **1b**,**c** in AcOH—H_2SO_4, pure products **2b,c** were isolated in the yields of 60 and 62%, respectively. In the case of compound **1a**, we succeeded to isolate both products by column chromatography (elution with $CHCl_3$). The attempts to reveal the effects of the concentrations of the starting compound and H_2SO_4 in the reaction mixtures **1a**—AcOH—H_2SO_4 (**1a** (0.45 g, 1.5 mmol) in the mixtures AcOH—H_2SO_4 with ratios of 2 : 0.1, 8 : 0.4, 4 : 0.1, 4 : 0.8, v/v) on the reaction course failed to give obvious information. It should be noted that both products in a ratio of *ca*. 1 : 1 were isolated from the reaction mixture obtained after refluxing compound **1a** in AcOH in the absence of H_2SO_4. A single crystal X-ray detraction analysis of the second product allowed us to unambiguously determine the structure of this product as **3a** (see Scheme 2, Fig. 1).

Table 1. Studies of chemical behavior of compound **1** (1.5 mmol) in a mixture of AcOH and H_2SO_4 (4 and 0.2 mL, respectively)

Compound	T_{solv}/°C[a]		Δ*t*/°C	τ[b]/min	Ratio[c] of
	bath	flask			**2** : **3**
1a	28	45	17	10	1 : 1
1b	40	50	10	10	1 : 0.6
1c	65	73	8	10	1 : 0.5
1d	85	87	2	10	1 : 0
1e	85	85	0	30	1 : 0
1f	85	91	6	10	1 : 0
1g	85	85	0	30	1 : 0

[aa] T_{solv} is temperature of dissolution of compound **1** (coincides with the reaction temperature).
[b] τ is the reaction time.
[c] ^{1}H NMR data.

According to X-ray diffraction analysis data, compound **3a** crystallizes with two independent molecules in the asymmetric unit of the orthorhombic unit cell; the independent molecules form H-bonded stable dimers (see Fig. 1). Bond lengths and geometry of the two molecules are almost the same. The only noticeable difference between two independent molecules is the dihedral angle between the planes of the phenyl ring and the bicyclic scaffold that is equal to 62.3(9)° for one molecule and 40.2(9)° for another. It is important that this difference in the geometry of the two molecules is not the result of the dynamic processes. The low-temperature measurements of the crystal of this compound (**3a_LT**) and molecular geometry analysis indicate that the difference between two molecules is retained even at −173 °C as it can be seen from Fig. 2 demonstrating the nominal overlap of two independent molecules. At −173 °C, the abovementioned dihedral angles are equal to 61.1(1)° and 40.7(1)°. It is notable that at both temperatures the differences between two independent molecules are almost the same. The presence of the strong electron withdrawing and electron donating groups predetermines the overall supramolecular crystal structure of compound **3a**. The main supramolecular synthons in crystal of **3a** are classical H-bonded dimers (see Fig. 1) that are connected *via* the N—H...O-

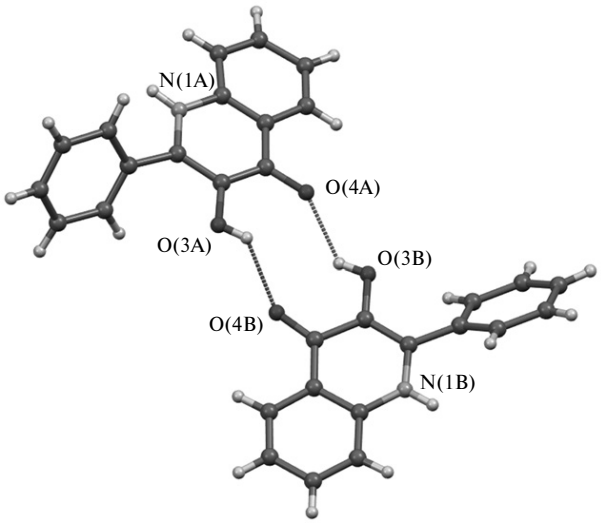


Fig. 1. Crystal geometry of two independent molecules in the crystal of compound **3a**. Nonhydrogen atoms are drawn as displacement ellipsoids at the 50% probability level, hydrogen atoms are drawn as spheres with arbitrary radii. The O—H...O hydrogen bonds in the dimer are shown by the dotted lines; the parameters of the H-bonds are as follows: *d*(O(3A)...O(4B)) = 2.87(2) Å, *d*(O(3B)...O(4A)) = 2.72(2) Å.

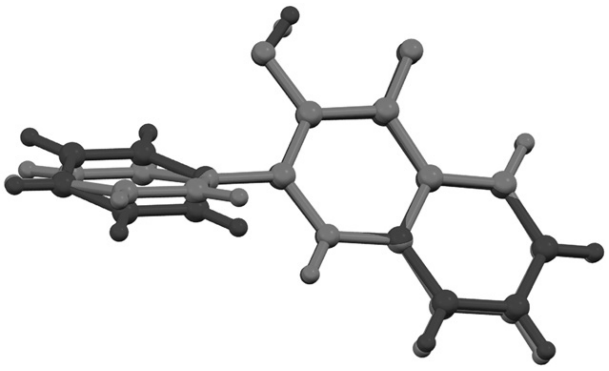


Fig. 2. Nominal overlap of two independent molecules **3a** in the crystal according to a low temperature experiment.

hydrogen bonds between the NH hydrogen atoms of the neighboring symmetrical H-bonded dimers into 2D supramolecular layer (Fig. 3). The final crystal packing of molecules **3a** is formed by parallel stacking of these 2D H-bonded layers along the 0*c* crystallographic axis. According to the earlier revealed regularity,[16,17] the H-bonded molecular layers are in the plane defined by the two smallest unit cell parameters (Fig. 4). In the crystal of **3a**, the voids potentially available for the solvate molecules were not found. The calculated packing factor is relatively high been equal to 68.3% and regularly increases to 69.6% with a decrease in experimental temperature to −173 °C.

Earlier,[16] we prepared compound having structure **3a** with identical physicochemical properties by acid hydro-

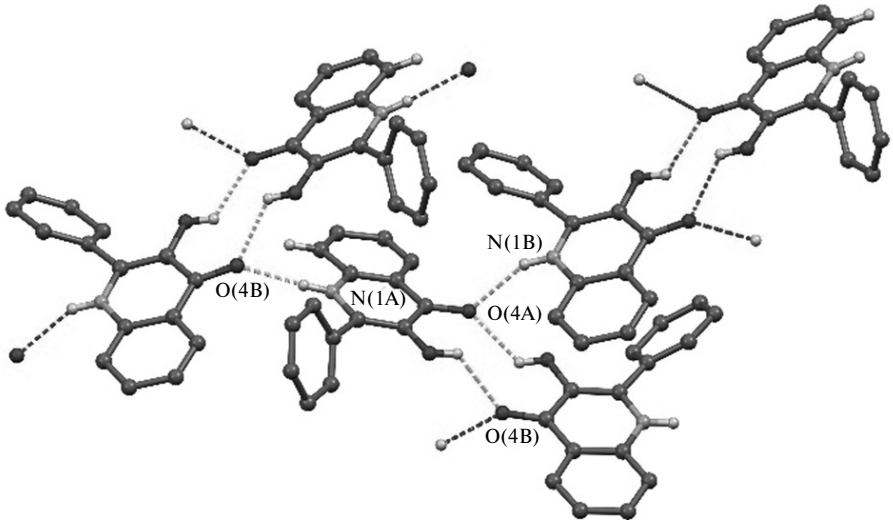


Fig. 3. Fragment of the system of classical H-bonds in the crystal of compound **3a** (only hydrogen atoms participating in the H-bonding are shown); parameters of the N...O interactions are as follows: d(N(1A)...O(4B′)) [1/2 + x, 3/2 − y, z] = 2.85(2) Å, d(O(4A)...N(1B″)) [1/2 + x, 1/2 − y, z] = 2.99(2) Å.

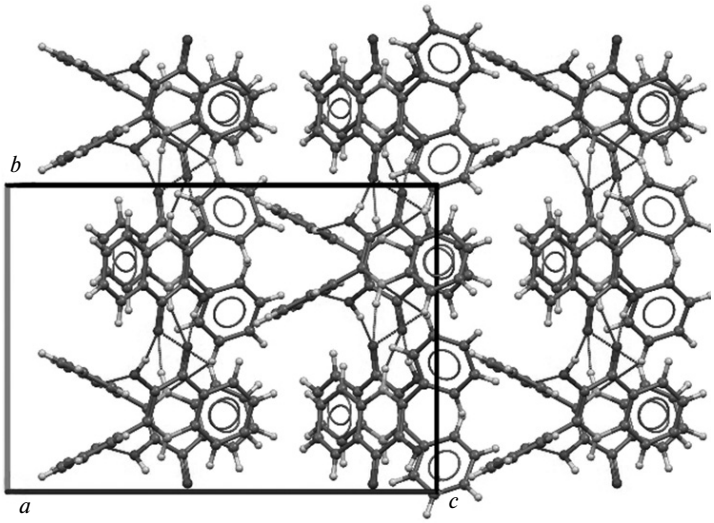
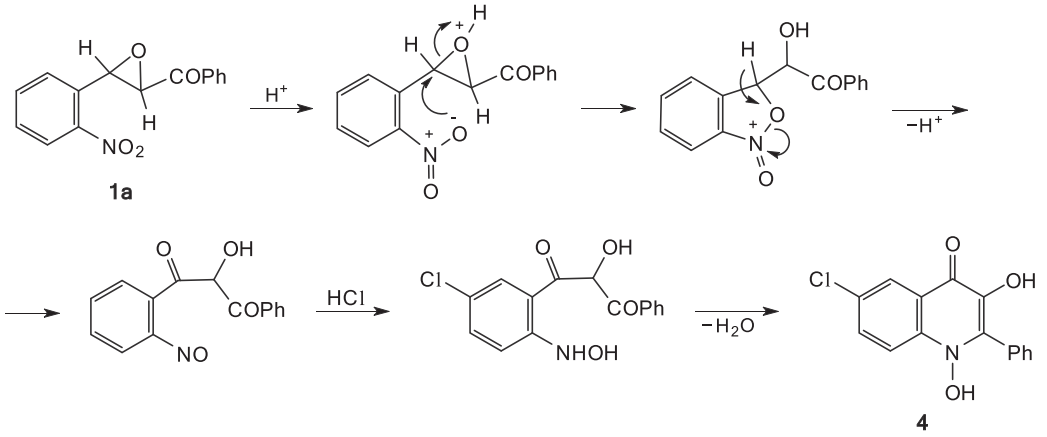


Fig. 4. View of the crystal packing of molecules **3a** along the 0*a* crystallographic axis.

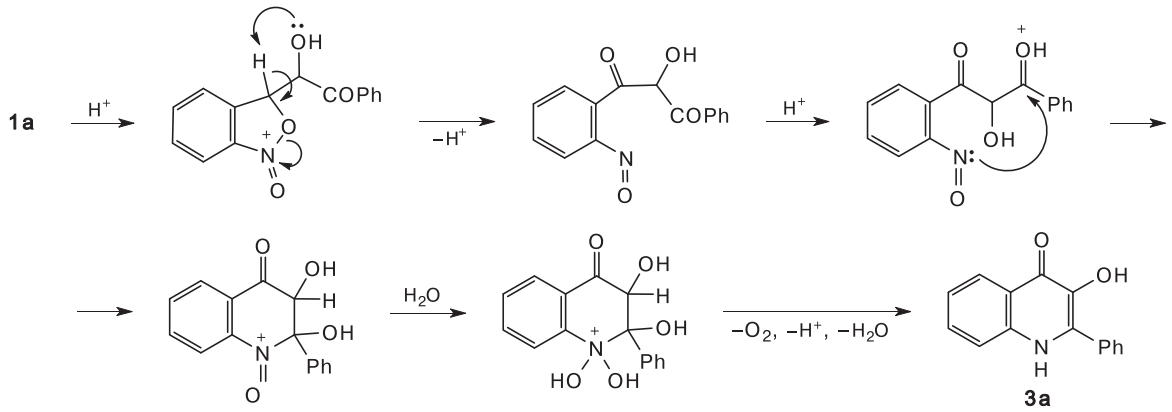
Scheme 3



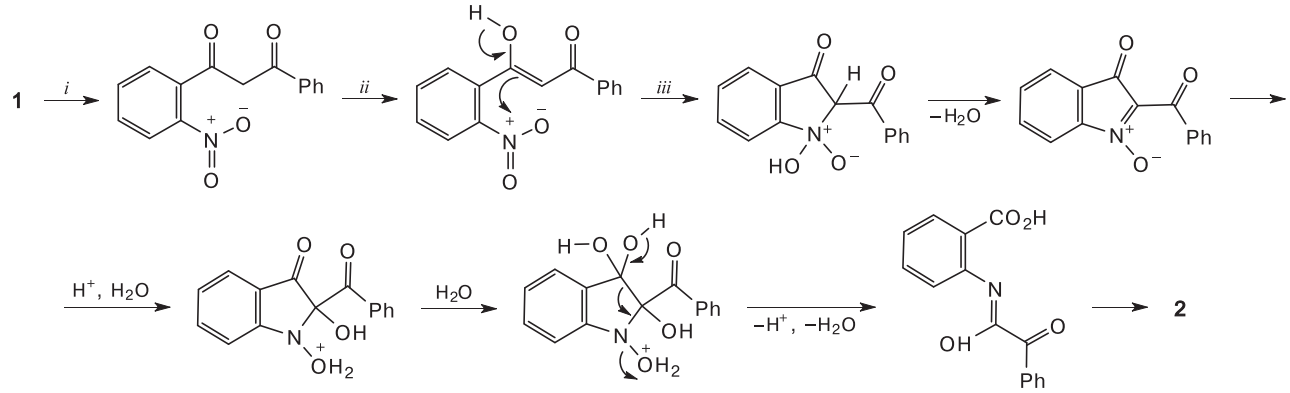
lysis of 4-bromo-3-hydroxy-2-phenylquinoline.[18—28] It is of note that only few methods for synthesizing 3-hydroxyquinolin-4-ones have been described. Among them, the synthesis of 6-chloro-1,3-dihydroxy-2-phenylquinolin-4-one (**4**) by treatment of [3-(2-nitroaryl)oxiran-2-yl](phenyl)methanone (**1a**) with ethereal hydrogen chloride is notable.[27,28] In our hands, this procedure gave the same results. Physicochemical properties of compound **4** are given in Experimental. The mechanism of the transformation of compound **1a** to product **4** is shown in Scheme 3.

Changing the reaction conditions, namely, heating the suspension of **1a** in an AcOH—H_2SO_4 mixture instead of

Scheme 4



Scheme 5



i. Meinwald rearrangement. *ii*, *iii.* Baeyer—Drewson type indigo synthesis.

a solution of **1a** in diethyl ether saturated with HCl, we obtained 1,6-unsubstituted 3-hydroxy-2-phenylquinolin-4-one (**3a**) along with anthranilic acid derivative **2a**. Quinolin-4-one **3a** is resulted from the loss of two oxygen atoms by the molecule of [3-(2-nitrophenyl)oxiran-2-yl]-(phenyl)methanone (**1a**). Taking into account this fact, we assume that compound **3a** is formed as shown in Scheme 4.

Mechanism of formation of anthranilic acid derivative **2** is adapted from our earlier work[12] (Scheme 5).

In summary, in the present work the chemical behavior of aryl 3-(2-nitroaryl)oxiran-2-yl ketones in acetic acid in the presence of sulfuric acid was studied and the possibility of the formation of the two types of compounds hardly available by other methods, *viz.*, 2-(2-oxy-2-arylacetamido)benzoic acids and 2-arylquinolin-4-one in the case of [3-(2-nitrophenyl)oxiran-2-yl](phenyl)methanone, was revealed.

Experimental

Melting points were measured with a Stuart SMP-10 apparatus. IR spectra were recorded on a Bruker Vector-22 spectrometer in KBr pellets. ^{1}H NMR spectra were run on Bruker Avance-400 (**1e—g**, **2a,b,d,e**), Bruker Avance-50 (**2f**), and Bruker Avance-600 (**2c,g**, **3a**, **4**) spectrometers in DMSO-d_6.

Aryl 3-(2-nitrophenyl)oxiran-2-yl ketones 1a—g were synthesized under the Darzens condensation conditions as earlier described[15] using 0.01 mmol of the starting compounds. Physicochemical properties of compounds **1a—d** are in agreement with those published earlier.[12,15]

Naphthalen-1-yl-[3-(2-nitrophenyl)oxiran-2-yl]methanone (1e). Yield 0.46 g (95%), m.p. 130—131 °C. Found (%): C, 71.62; H, 3.91; N, 4.22. $C_{19}H_{13}NO_4$. Calculated (%): C, 71.47; H, 4.10; N, 4.39. IR, ν/cm^{-1}: 1684, 1521, 1343. ^{1}H NMR, δ: 4.57, 4.63 (both d, 1 H each, H_{ox}, J = 1.9 Hz)*; naphthyl + C_6H_4: 7.58—7.72 (m, 5 H), 7.84 (dd, 1 H, J = 7.4 Hz, J = 7.4 Hz), 8.03 (d, 1 H, J = 7.4 Hz), 8.17 (d, 1 H, J = 7.5 Hz), 8.21 (dd, 2 H, J = 7.2 Hz, J = 7.5 Hz), 8.56 (d, 1 H, J = 8.5).

[3-(5-Chloro-2-nitrophenyl) oxiran-2-yl](4-methoxyphenyl)-methanone (1f). Yield 2.87 g (96%), m.p. 153—154 °C. Found (%): C, 57.64; H, 3.41; Cl, 10.78; N, 4.09. $C_{16}H_{12}ClNO_5$. Calculated (%): C, 57.58; H, 3.63; Cl, 10.62; N, 4.20. IR, ν/cm^{-1}: 1678, 1599, 1512, 1340, 1242, 839. ^{1}H NMR, δ: 3.85 (s, 3 H, OMe); 4.55, 4.73 (both br.s, 1 H each, H_{ox}); 7.06, 8.06 (both d, 2 H each, C_6H_4, J = 8.7 Hz); 7.57 (s, 1 H, H(6), C_6H_3); 7.72, 8.22 (both d, 1 H each, H(3), H(4), C_6H_3, J = 8.4 Hz).

(4-Chlorophenyl)[3-(2,4-dinitrophenyl)oxiran-2-yl]methanone (1g). Yield 13.38 g (97%), m.p. 154—155 °C. Found (%): C, 51.73; H, 3.01; Cl, 10.12; N, 15.62. $C_{15}H_9ClN_2O_6$. Calculated (%): C, 51.66; H, 2.61; Cl, 10.17; N, 15.55. IR, ν/cm^{-1}: 1683, 1531, 1348. ^{1}H NMR, δ: 4.70, 4.82 (both d, 1 H each, H_{ox}, J = 4.0 Hz); 7.64, 8.11 (both d, 2 H each, C_6H_4, J = 8.5 Hz); 7.88 (d, 1 H, H(6), C_6H_3, J = 8.6 Hz); 8.65 (dd, 1 H, H(5), C_6H_3, J = 8.6 Hz, J = 2.3 Hz); 8.85 (d, 1 H, H(3), C_6H_3, J = 2.3 Hz).

Studies of the chemical behavior of aryl 3-(2-nitroaryl)oxiran-2-yl ketones 1a—g in acidic medium. ***Experiment 1.*** A two-neck flask charged with compound **1** (1.5 mmol) and equipped with a thermometer and a refluxing condenser was placed into a water bath equipped with a thermometer. When a mixture of AcOH (4 mL) and H_2SO_4 (0.2 mL) was added to compound **1**. The mixture was slowly heated under stirring and temperatures of both the bath and the mixture corresponding to the complete dissolution of compound **1** were detected. Stirring at this temperature was continued for 10 min in the case of compounds **1a—d,f** and for 30 min in the case of compounds **1e,g**. The reaction mixtures were poured into water (75 mL). In the case of compounds **1a,b**, heavy dark-brown oils were precipitated, which were washed by decantation with water (3×25 mL), and air dried. ^{1}H NMR spectra of these oils show the signals of compounds **2a,b** and **3a,b** in the ratios of 1 : 1 and 1 : 0.6, respectively. Column chromatography (silica gel 40 A, elution with $CHCl_3$) afforded pure compounds **2a**,**b** and **3a**. In the case of compounds **1c—g**, the precipitates formed were collected by filtration, washed with water (2×15 mL), and dried. ^{1}H NMR spectra of the crude products obtained from compounds **1d,e—g** revealed the signals of compounds **2d,e—g**. These compounds were purified by washings with diethyl ether (2×8 mL). In the case of the crude product obtained from compound **1c**, ^{1}H NMR spectrum exhibited signals of compounds **2c** and **3c** in a 1 : 0.6 ratio. Compound **2c** was isolated pure by column chromatography (silica gel 40 A, elution with $CHCl_3$).

2-(2-Oxo-2-phenylacetamido)benzoic acid (2a). Yield 0.14 g (35%), m.p. 184—185 °C. Found (%): C, 66.83; H, 4.23; N, 5.32. $C_{15}H_{11}NO_4$. Calculated (%): C, 66.91; H, 4.12; N, 5.20. IR, ν/cm^{-1}: 1699, 1670, 1583, 1519, 1258. ^{1}H NMR, δ: 7.29, 7.74 (both dd, 1 H each, H(4), H(5), NC_6H_4, J = 7.5 Hz, J = 7.7 Hz); 7.59 (dd, 2 H, H(3), H(5), C_6H_4, J = 7.8 Hz, J = 7.8 Hz); 7.70 (dd, 1 H, H(4), C_6H_4, J = 7.8 Hz, J = 7.8 Hz); 8.06, 8.63 (both d, 1 H each, H(3), H(6), NC_6H_4, J = 7.6 Hz, J = 7.8 Hz); 8.21 (d, 2 H, H(2), H(6), C_6H_4, J = 7.9 Hz); 12.38 (s, 1 H, NH).

3-Hydroxy-2-phenylquinolin-4(1*H*)-one (3a). Yield 0.14 g (40%), m.p. 269—270 °C (*cf.* Ref. 18: 270—271 °C). Found (%): C, 75.81; H, 4.45; N, 5.79. $C_{15}H_{11}NO_2$. Calculated (%): C, 75.94; H, 4.67; N, 5.90. IR, ν/cm^{-1}: 3241, 1632, 1549, 1487, 1402, 1368, 1267. ^{1}H NMR, δ: 7.28, 7.58 both dd, 1 H each, H(6), H(7), H_{quin}, J = 7.2 Hz, J = 7.8 and J = 7.2 Hz, J = 6.8 Hz)**; 7.45—7.75 (m, 5 H, Ph); 7.78, 8.17 (both d, 1 H each, H(5), H(8), H_{quin}, J = 6.7 Hz and J = 7.9 Hz); 11.70 (br.s, 1 H, NH).

2-[2-Oxo-2-(*p*-tolyl)acetamido]benzoic acid (2b). Yield 0.25 g (60%), m.p. 200—201 °C (*cf.* Ref. 12: 199—201 °C). Found (%): C, 67.73; H, 4.51; N, 4.76. $C_{16}H_{13}NO_4$. Calculated (%): C, 67.84; H, 4.63; N, 4.94. IR, ν/cm^{-1}: 1699, 1678, 1668, 1584, 1524, 1266, 754. ^{1}H NMR, δ: 2.41 (s, 3 H, Me); 7.27, 7.68 (both dd, 1 H each, H(4), H(5), NC_6H_4, J = 7.6 Hz, J = 7.6 Hz); 7.39, 8.14 (both d, 2 H each, C_6H_4, J = 7.7 Hz); 8.05, 8.64 (both d, 1 H each, H(3), H(6), NC_6H_4, J = 7.6 Hz); 12.35 (s, 1 H, NH).

2-[2-(4-Methoxyphenyl)-2-oxoacetamido]benzoic acid (2c). Yield 0.28 g (62%), m.p. 211—212 °C (*cf.* Ref. 12: 178—181 °C). Found (%): C, 64.13; H, 4.42; N, 4.53. $C_{16}H_{13}NO_5$. Calculated (%): C, 64.21; H, 4.38; N, 4.68. IR, ν/cm^{-1}: 1701, 1675, 1601, 158, 1528, 1263, 753. ^{1}H NMR, δ: 3.87 (s, 3 H, OMe); 7.10, 8.26 (both d, 2 H each, C_6H_4, J = 8.9 Hz); 7.27, 7.68 (both dd, 1 H each, H(4), H(5), NC_6H_4, J = 7.2 Hz, J = 7.1 Hz); 8.05, 8.62 (both d, 1 H each, H(3), H(6), NC_6H_4, J = 7.2 Hz); 12.34 (s, 1 H, NH).

* H_{ox} stands for the oxirane ring protons.

** H_{quin} stands for the quinoxaline ring protons.

2-[2-(4-Chlorophenyl)-2-oxoacetamido]benzoic acid (2d). Yield 0.35 g (78%), m.p. 199—200 °C. Found (%): C, 59.63; H, 3.50; Cl, 11,37; N, 4.55. $C_{15}H_{10}ClNO_4$. Calculated (%): C, 59.32; H, 3.32; Cl, 11,67; N, 4.61. IR, ν/cm^{-1}: 1698, 1682, 1671, 1584, 1542, 1263. ^{1}H NMR, δ: 7.29, 7.70 (both dd, 1 H each, H(4), H(5), NC_6H_4, J = 7.6 Hz, J = 7.6 Hz); 7.66, 8.25 (both d, 2 H each, C_6H_4, J = 8.4 Hz); 8.07, 8.65 (both d, 1 H each, H(3), H(6), NC_6H_4, J = 7.7 Hz); 12.44 (s, 1 H, NH).

2-[2-(Naphthalen-1-yl)-2-oxoacetamido]benzoic acid (2e). Yield 0.34 g (72%), m.p. 213—215 °C. Found (%): C, 71.53; H, 4.22; N, 4.43. $C_{19}H_{13}NO_4$. Calculated (%): C, 71.47; H, 4.10; N, 4.39. IR, ν/cm^{-1}: 1682, 1586, 1509, 1233. ^{1}H NMR, δ: 7.30 (dd, 1 H, H(4), NC_6H_4, J = 7.6 Hz, J = 7.8 Hz); 7.59—7.75 (m, 4 H), 8.09 (dd, 2 H, J = 7.6 Hz, J = 7.8 Hz), 8.26 (dd, 2 H, J = 6.2 Hz, J = 6.4 Hz), 8.48 (d, 1 H, J = 8.3 Hz) — naphthyl + + H(3), H(5), NC_6H_4; 8.67 (d, 1 H, H(6), NC_6H_4, J = 8.3 Hz); 12.55 (s, 1 H, NH).

5-Chloro-2-[2-(4-methoxyphenyl)-2-oxoacetamido]benzoic acid (2f). Yield 0.42 g (84%), m.p. 245—246 °C. Found (%): C, 57.48; H, 3.41; Cl, 10.22; N, 4.44. $C_{16}H_{12}ClNO_5$. Calculated (%): C, 57.60; H, 3.63; Cl, 10.63; N, 4.20. IR, ν/cm^{-1}: 1702, 1681, 1598, 1577, 1510, 1250, 1158. ^{1}H NMR, δ: 3.87 (s, 3 H, OMe); 7.09, 8.24 (both d, 2 H each, C_6H_4, J = 8.9 Hz); 7.72 (dd, 1 H, H(4), C_6H_3, J = 8.9 Hz, J = 2.4 Hz); 7.96 (d, 1 H, H(6), C_6H_3, J = 2.4 Hz); 8.61 (d, 1 H, H(3), C_6H_3, J = 8.8 Hz); 12.27 (s, 1 H, NH).

2-[2-(4-Chlorophenyl)-2-oxoacetamido]-4-nitrobenzoic acid (2g). Yield 0.40 g (77%), m.p. 283—284 °C. Found (%): C, 51.52; H, 2.47; Cl, 10.24; N, 8.432. $C_{15}H_9ClN_2O_6$. Calculated (%): C, 51.67; H, 2.60; Cl, 10.17; N, 8.03. IR, ν/cm^{-1}: 1703, 1675, 1529, 1512,1255, 993. ^{1}H NMR, δ: 7.67, 8.28 (both d, 2 H each, C_6H_4, J = 8.0 Hz); 8.05, 8.29 (both d, 1 H each, H(5), H(6), C_6H_3, J = 7.8 Hz); 9.46 (s, 1 H, H(3), C_6H_3); 12.59 (s, 1 H, NH).

Experiment 2. Through a solution of compound **1a** (0.40 g, 1.5 mmol) in diethyl ether (250 mL) cooled to 0—5 °C, dry gaseous HCl was slowly bubbled for 3 h. The precipitate formed after removal of ~1/3 of the solvent under the reduced pressure was collected by filtration and dried to afford 0.31 g (73%) of **4**, m.p. 263—264 °C (*cf.* Ref. 28: 270 °C; *cf.* Ref. 29: 264 °C). Found (%): C, 62.59; H, 3.22; Cl, 12.48, N, 4.63. $C_{15}H_{10}ClNO_3$. Calculated (%): C, 62.62; H, 3.50; Cl, 12.32; N, 4.87. IR, ν/cm^{-1}: 3434, 3073, 2689, 1582, 1386, 1371, 688. ^{1}H NMR, δ: 7.46—7.52 (m, 5 H, Ph); 7.75 (dd, 1 H, H(7), J = 9.2 Hz, J = 2.1 Hz); 7.93 (d, 1 H, H(8), J = 9.2 Hz); 8.21 (d, 1 H, H(5), J = 2.0 Hz).

Single crystal X-ray diffraction analysis of compound **3a** was performed with a Bruker Kappa Apex II CCD automated system (λ(Mo-Kα) = 0.71073 Å, graphite monochromator, φ and ω scan modes) at 23 °C (**3a**) and −173 °C (**3a_LT**). The data were collected, processed, and the unit cell parameters were refined using APEX2 software.[30] Semiempirical absorption corrections were applied using SADABS program.[31]. The structure was solved by the direct method and refined by the full-matrix least-squares

Table 2. Crystallographic parameters and X-ray data collection and structure refinement statistics for compounds **3a**_LT and **3a**

Parameter	**3a**_LT	**3a**
Molecular formula	$C_{15}H_{11}NO_2$	$C_{15}H_{11}NO_2$
Crystal habit	Prismatic	Prismatic
M/g mol^{-1}	237.25	237.25
T/K	100(2)	296(2)
Crystal system	Orthorhombic	Orthorhombic
Space group	$Pna2_1$	$Pna2_1$
Crystal size/mm^3	0.322×0.423×0.595	0.272×0.183×0.121
Z	8	8
Unit cell parameters		
a/Å	9.8536(10)	9.889(8)
b/Å	12.9367(12)	13.027(10)
c/Å	18.0722(16)	18.189(14)
V/Å^3	2303.7(4)	2343(3)
F(000)	992	992
d_{calc}/g cm^{-3}	1.368	1.345
μ/mm^{-1}	0.092	0.090
θ/deg	1.94 ≤ θ ≤ 28.38	1.92 ≤ θ ≤ 27.24
Number of measured reflections	32657	17651
Number of independent reflections	5651	4952
R_{int}	0.0679	0.1541
Number of reflections with $I > 2\sigma(I)$	4286	1089
Number of refinement parameters for all reflections with $I > 2\sigma(I)$	331	325
R_1	0.0526	0.0992
wR_2	0.1391	0.1758
GOOF on F^2	1.025	0.889
Residual electron density (ρ_{max}/ρ_{min})/e Å^{-3}	0.265/−0.238	0.374/−0.354

method first in isotropic and then in anisotropic approximations (for all non-hydrogen atoms) with SHELXL program.[32] The positions of hydrogen atoms were calculated based on stereochemical considerations and refined using the corresponding riding models. All calculations were performed with WinGX program.[33] The intermolecular interactions were analyzed and the molecular structures and crystal packing diagrams were drawn using PLATON[34] and Mercury[35] software. Crystallographic data found at 23 °C (**3a**) and −173 °C (**3a_LT**) and the parameters of X-ray diffraction experiment are given in Table 2.

The atomic coordinates and structural parameters of compound **3a** at 23 °C (**3a**) and −173 °C (**3a_LT**) were deposited with the Cambridge Crystallographic Data Centre (CCDC 1958154, 1958155) and are available free of charge at www.ccdc.cam.ac.uk/data_request/cif.

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