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Quinone Imines with a Fused Azine Ring: II.* Reaction of 5-(*p*-Tolylsulfonylimino)quinoline-8(5*H*)-ones with Sodium *p*-Toluenesulfinate

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Abstract—Depending on the substituent in the 7-position, 5-(p-tolylsulfonylimino)quinoline-8(5*H*)-ones react with sodium *p*-toluenesulfinate in acetic acid along three different pathways: 1,4- or 6,1-addition or nucleophilic substitution.

In the preceding communication [1] we reported on hitherto unknown 5-arylsulfonyliminoquinolin-8-ones. Using 5-(*p*-tolylsulfonylimino)quinolin-8(5*H*)-one (**I**) as an example, we considered methods of synthesis of such compounds and found that it reacts with hydrogen chloride following the 1,4-addition pattern to give 7-chloro derivative **II** as the corresponding hydrochloride (Scheme 1). It should be noted that reactions of N-substituted quinone imines with chloride ion (which is a hard nucleophile) involve intermediate formation of mono- and diprotonated substrate species [2, 3] and that arenesulfinate ion as a mild nucleophile reacts directly with the neutral substrate via one-electron transfer [4].

The goal of the present work was to examine the reaction of 5-(*p*-tolylsulfonylimino)quinolin-8(5*H*)-ones with sodium *p*-toluenesulfinate. Treatment of quinone imine **I** with sodium *p*-toluenesulfinate dihydrate in glacial acetic acid afforded 8-hydroxy-7-(*p*-tolylsulfonyl)-5-(*p*-tolylsulfonylamino)quinoline (**III**). The position of the second tosyl group was determined by a series of consecutive transformations of the product. Oxidation of **III** with (diacetoxyiodo)-benzene in acetic acid gave unstable 7-(*p*-tolylsulfonyl)-5-(*p*-tolylsulfonylimino)quinolin-8(5*H*)-one (**A**), which was treated *in situ* with an equimolar amount of sodium *p*-toluenesulfinate dihydrate to obtain the terminal addition product, 8-hydroxy-7-(*p*-tolylsulfonyl)-5-[bis(*p*-tolylsulfonyl)amino]quinoline (**IV**) (Scheme 1).

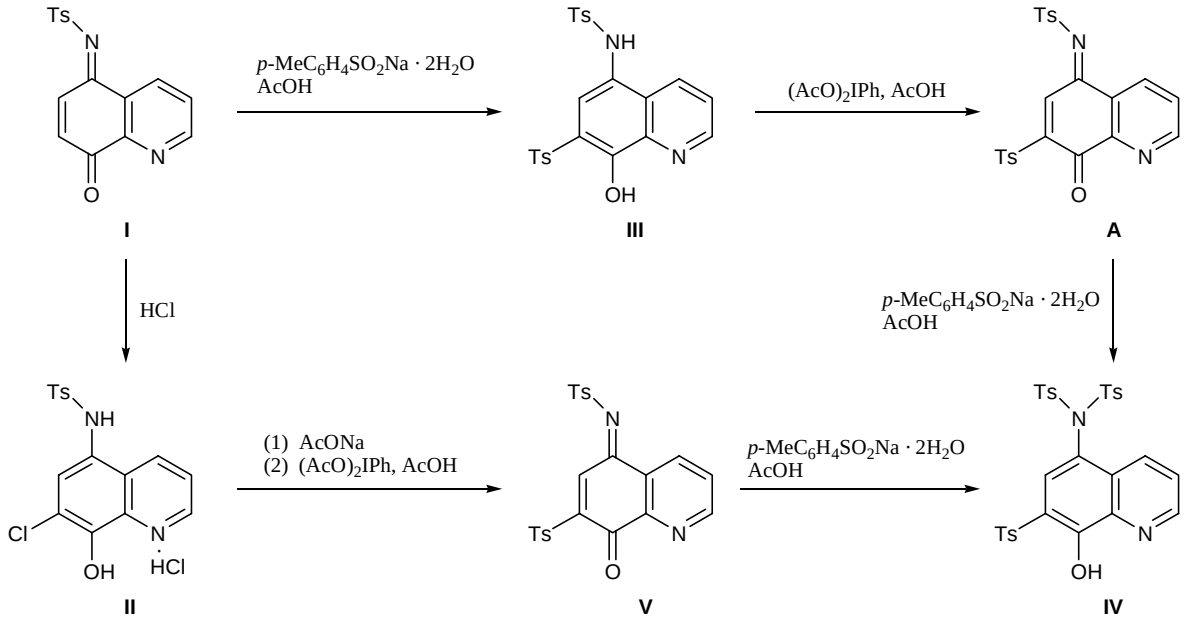
Oxidation of hydrochloride **II** with (diacetoxyiodo)benzene in acetic acid (after preliminary treatment of the reaction mixture with an equivalent amount of anhydrous sodium acetate) led to formation of 7-chloro-5-(*p*-tolylsulfonylimino)quinolin-8(5*H*)-one (**V**). The latter reacted with sodium *p*-toluenesulfinate dihydrate, regardless of the reactant ratio, yielding the substitution–addition product (nucleophilic substitution of the 7-chlorine atom was followed by terminal addition) which was identical to compound **IV**. We failed to detect intermediate substitution product **A** by chromatography, though analogous products of chlorine replacement in 2-chloro-4-arylsulfonyliminonaphthalen-1(4*H*)-ones were isolated [5, 6]. The structure of compounds **III**–**V** was confirmed by elemental analysis and ^{1}H NMR and IR spectroscopy.

Taking into account that quinone imines **I** and **V** are fairly readily soluble in acetic acid, in order to increase the yields of compounds **III** and **IV** we propose a procedure acording to which sodium *p*-toluenesulfinate dihydrate is added directly to a solution of freshly prepared quinone imine in acetic acid.

Our results led us to the following conclusions: (1) 5-(*p*-tolylsulfonylimino)quinolin-8(5*H*)-one having no substituents in positions *6* and *7* reacts with sodium *p*-toluenesulfinate in acetic acid according to the 1,4-addition pattern with formation of the corresponding 7-substituted dihydro derivative; (2) the chlorine atom in 7-chloro-5-(*p*-tolylsulfonylimino)-quinolin-8(5*H*)-one is readily replaced by *p*-tolylsulfonyl group; and (3) the presence of a tosyl group in position *7* of 5-(*p*-tolylsulfonylimino)quinolin-8(5*H*)-one gives rise to formation of the 6,1-addition product

* For communication I, see [1].

Scheme 1.



in the reaction with *p*-toluenesulfinate ion. The above chemical transformations are important from the synthetic viewpoint, for they open the way to difficultly accessible 7-arylsulfonyl-substituted quinoline derivatives.

EXPERIMENTAL

The IR spectra were recorded on a UR-20 instrument from samples pelleted with KBr. The ^{1}H NMR spectra were obtained on a Varian VXR-300 spectrometer (299.945 MHz) from 5% solutions in DMSO-d_6 using TMS as internal reference. The purity of the products was checked by TLC on Silufol plates using $CHCl_3$–MeOH–NH_3 (100:10:1) or $CHCl_3$–MeOH–AcOH (100:10:1) as eluent, development with UV light (compounds **III** and **IV**); or on Al_2O_3 plates with ethyl acetate as eluent (compound **V**).

8-Hydroxy-7-(*p*-tolylsulfonyl)-5-(*p*-tolylsulfonylamino)quinoline (III). Sodium *p*-toluenesulfinate dihydrate, 1.1 g (5.1 mmol), was added with stirring to a suspension of quinone imine **I**, prepared from 1.5 g (4.3 mmol) of 8-hydroxy-5-(*p*-tolylsulfonylamino)quinoline hydrochloride [1], in 25 ml of glacial acetic acid. The mixture was stirred for 45 min, and the finely crystalline precipitate was filtered off, washed with glacial acetic acid and hexane, and dried at 55–60°C. Yield 1.9 g [94%, calculated on the initial 8-hydroxy-5-(*p*-tolylsulfonylamino)quinoline hydrochloride); bright yellow powder, mp 228–229°C (decomp., from AcOH. IR spectrum, ν, cm^{-1}: 1320, 1160 (SO_2); 3245 (NH). ^{1}H NMR spectrum, δ, ppm: 2.379 s (3H, 4-C**H**$_3$C$_6$H$_4$N), 2.411 s (3H, 4-C**H**$_3$-C$_6$H$_4$C), 7.376 s (1H, 6-H), 7.389 d (2H, H$_A$ in 4-CH$_3$-C$_6$H$_4$N, J = 8.1 Hz), 7.416 d (2H, H$_A$ in 4-CH$_3$C$_6$H$_4$C, J = 8.1 Hz), 7.531 d (2H, H$_B$ in 4-CH$_3$C$_6$H$_4$N, J = 8.1 Hz), 7.605 d (2H, H$_B$ in 4-CH$_3$C$_6$H$_4$C, J = 8.1 Hz), 7.725 d.d (1H, 3-H, J_1 = 3.9, J_2 = 7.5 Hz), 8.521 d.d (1H, 4-H, J_1 = 3.0, J_2 = 7.5 Hz), 8.910 d.d (1H, 2-H, J_1 = 3.0, J_2 = 3.9 Hz), 10.077 s (1H, NH). Found, %: N 6.02; S 13.28. $C_{23}H_{20}N_2O_5S_2$. Calculated, %: N 5.98; S 13.69.

7-Chloro-5-(*p*-tolylsulfonylimino)quinolin-8(5*H*)-one (V). (Diacetoxyiodo)benzene, 0.84 g (2.6 mmol), was added with stirring to a suspension of 1 g (2.6 mmol) of hydrochloride **II** [1] and 0.21 g (2.6 mmol) of anhydrous sodium acetate in 11 ml of glacial acetic acid. After 3 h, the precipitate was filtered off, washed with glacial acetic acid and hexane, and dried in a vacuum desiccator. Yield 0.84 g (93%), greenish–yellow needles, mp 240–242°C (decomp., from toluene). IR spectrum, ν, cm^{-1}: 1308, 1150 (SO_2); 1681 (C=O, C=N). ^{1}H NMR spectrum, δ, ppm: 2.449 s (3H, 4-C**H**$_3$C$_6$H$_4$), 7.528 d (2H, H$_A$ in 4-CH$_3$C$_6$H$_4$, J = 7.8 Hz), 7.973 d (2H, H$_B$ in 4-CH$_3$-C$_6$H$_4$, J = 7.8 Hz), 8.433 s (1H, 6-H), 7.789 d.d (1H, 3-H, J_1 = 4.8, J_2 = 8.4 Hz), 8.419 d.d (1H, 4-H, J_1 = 3.3, J_2 = 8.4 Hz), 9.011 d.d (1H, 2-H, J_1 = 3.3, J_2 = 4.8 Hz). Found, %: N 7.99; S 9.16. $C_{16}H_{11}ClN_2O_3S$. Calculated, %: N 8.08; S 9.25.

8-Hydroxy-7-(*p*-tolylsulfonyl)-5-[bis(*p*-tolylsulfonyl)amino]quinoline (IV). *a*. Quinoline **III**, 1 g (2.1 mmol), was added to a suspension of 0.28 g (2.1 mmol) of (diacetoxyiodo)benzene in 8 ml of glacial acetic acid. The mixture was stirred for 4.5 h, and 0.5 g (2.3 mmol) of sodium *p*-toluenesulfinate dihydrate was added. The suspension was stirred for 2 h and was then left to stand for 24 h. The precipitate was filtered off, washed with glacial acetic acid and hexane, and dried at 55–60°C. Yield 0.77 g (58%, calculated on the initial dihydro derivative **III**); bright yellow powder, mp 241–243°C (decomp., from acetic acid).

b. Sodium *p*-toluenesulfinate dihydrate, 1.5 g (7 mmol), was added with stirring to a mixture containing quinone imine **V** which was prepared as described above by oxidation of 1 g (2.6 mmol) of compound **II**. The mixture was stirred for 5 h at room temperature and was left to stand for 24 h. The product was isolated as described above in *a*. Yield 1.6 g (quantitative, calculated on **II**); bright yellow powder, mp 243–244°C (decomp.). The product showed no depression of the melting point on mixing with a sample prepared as described in *a*. IR spectrum, ν, cm^{-1}: 1369, 1172 (SO_2). ^1H NMR spectrum, δ, ppm: 2.399 s (3H, 4-C**H**$_3C_6H_4C$), 2.494 s (6H, 4-C**H**$_3$-C_6H_4N), 7.341 s (1H, 6-H), 7.480 d (2H, H_A in 4-CH_3-C_6H_4C, J = 8.7 Hz), 7.532 d (4H, H_A in 4-$CH_3C_6H_4N$, J = 8.7 Hz), 7.675 d (4H, H_B in 4-$CH_3C_6H_4N$, J = 8.7 Hz), 7.731 d (2H, H_B in 4-$CH_3C_6H_4C$, J = 8.7 Hz), 7.759 d.d (1H, 3-H, J_1 = 4.4, J_2 = 8.4 Hz), 7.952 d.d (1H, 4-H, J_1 = 3.9, J_2 = 8.4 Hz), 8.956 d.d (1H, 2-H, J_1 = 3.9, J_2 = 4.4 Hz). Found, %: N 4.42; S 15.41. $C_{30}H_{26}N_2O_7S_3$. Calculated, %: N 4.50; S 15.45.

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