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SHORT COMMUNICATIONS

Reactions of *N,N′*-Bis(methoxycarbonyl)-*p*-benzoquinonediimine with β-Tosyl Carbonyl Compounds

A. V. Velikorodov and V. B. Mochalin

Astrakhan State Pedagogical University, ul. Tatishcheva 20a, Astrakhan, 414056 Russia
e-mail: astpedun@astranet.ru

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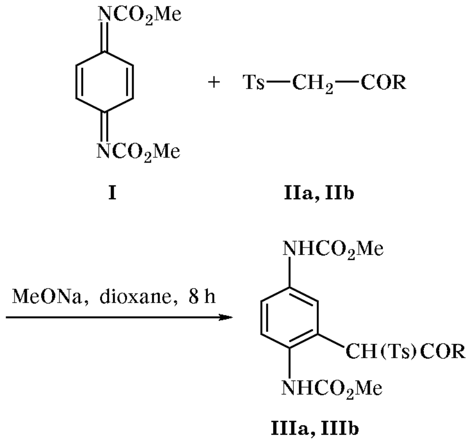
Reactions of mono- and disulfonyl derivatives of benzoquinonimines with various β-dicarbonyl compounds have been well documented [1]. We reported in [2] on the synthesis of carbamate indole derivatives from the corresponding Michael adducts of *N,N′*-bis(methoxycarbonyl)-*p*-benzoquinonediimine (**I**) and β-diketones or β-keto esters. There are almost no published data on reactions of β-sulfonyl carbonyl compounds with quinoid structures [3, 4]. On the other hand, β-sulfonyl ketones are fairly strong CH acids (p*K* ~10) [5]. With the goal of obtaining new polyfunctional carbamate derivatives of indole (which attract interest from the viewpoint of biological activity), in the present work we examined reactions of compound **I** with tosylacetone (**IIa**), tosylacetophenone (**IIb**), and ethyl tosylacetate (**IIc**) in dioxane at 20°C in the presence of sodium methoxide.

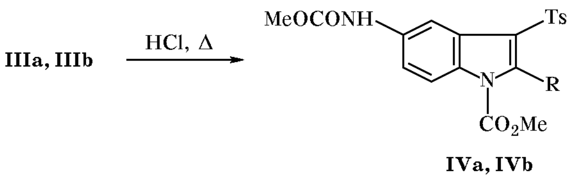
According to the data of elemental analysis and IR spectroscopy, the products were the corresponding Michael adducts **IIIa** and **IIIb**:



II, **III**, R = Me (**a**), Ph (**b**).

Unlike initial quinonediimine **I**, compounds **III** showed in the IR spectra absorption bands at 3330–3335 cm^{-1} due to stretching vibrations of the NH group, 1600–1515 cm^{-1} (C=C$_{arom}$), and 1140–1145 and 1310–1315 cm^{-1} (antisymmetric and symmetric vibrations of the sulfonyl group).

We failed to obtain the corresponding Michael adduct from quinonediimine **I** and ethyl tosylacetate (**IIc**) in dioxane or benzene in the presence of MeONa or Et$_3$N. In all cases, strong tarring occurred. By heating adducts **IIIa** and **IIIb** in 22% hydrochloric acid for 1.5 h [2] we synthesized indole derivatives **IVa** and **IVb** whose structure was confirmed by the ^{1}H NMR spectra.



IV, R = Me (**a**), Ph (**b**).

We also examined the possibility for synthesizing indoles **IVa** and **IVb** in one step, following the procedure reported in [2]. As with β-diketones, the reaction of **I** with β-tosyl ketones **IIa** and **IIb** stopped at the stage of formation of the corresponding 1,4-bis(methoxycarbonylamino)benzenes **IIIa** and **IIIb** in 69 and 71% yield, repsectively.

Tosyl derivatives **IIa**–**IIc** were prepared by heating in ethanol for 6 h at 70°C equimolar amounts of sodium *p*-toluenesulfinate dihydrate [6] and chloroacetone [7], phenacyl bromide, or ethyl chloroacetate [6], respectively. Tosylacetone (**IIa**): yield 55%, mp 52°C (published data [8]: mp 52–54°C); tosyl-

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acetophenone (**IIb**): yield 72%, mp 110°C (published data [8]: mp 109–110°C); ethyl tosylacetate (**IIc**): yield 63%, mp 34°C (from diethyl ether). Found, %: C 54.32; H 6.01; S 13.11. $C_{11}H_{14}O_4S$. Calculated, %: C 54.55; H 5.79; S 13.22.

1,4-Bis(methoxycarbonylamino)-2-(2-oxo-1-tosylpropyl)benzene (IIIa). To a solution of 4.5 mmol of quinonediimine **I** in 10 ml of anhydrous dioxane we added 4.6 mmol of ketone **IIa** and 0.04 g of sodium methoxide, the mixture was kept for 8 h at 20°C, 2–3 drops of glacial acetic acid was added, and the mixture was poured into 100 ml of water. The precipitate was filtered off, dried in air, and recrystallized from ethanol. Yield 72%, mp 148°C. Found, %: C 54.85; H 5.34; N 6.66. $C_{20}H_{22}N_2O_7S$. Calculated, %: C 55.30; H 5.07; N 6.45.

1,4-Bis(methoxycarbonylamino)-2-(2-oxo-2-phenyl-1-tosylethyl)benzene (IIIb) was synthesized in a similar way. Yield 89%, mp 132°C. Found, %: C 60.67; H 4.51; N 5.72. $C_{25}H_{24}N_2O_7S$. Calculated, %: C 60.48; H 4.84; N 5.65.

Methyl 5-methoxycarbonylamino-3-tosylindole-1-carboxylate (IVa). A suspension of 2.3 mmol of adduct **IIIa** in 20 ml of 22% hydrochloric acid was refluxed for 1.5 h. It was then cooled, and the precipitate was filtered off, dried in air, and recrystallized from glacial acetic acid. Yield 76%, mp 163°C. ^{1}H NMR spectrum, δ, ppm: 8.72 br.s (1H, NH), 8.49 s (1H, 4-H), 7.98 d (1H, H_{arom}, J = 11 Hz), 7.65 d (1H, H_{arom}, J = 11 Hz), 7.34 d (2H, H_{arom}, J = 10 Hz), 7.22 d (2H, H_{arom}, J = 10 Hz), 3.79 s (3H, OMe), 3.68 s (3H, OMe), 2.80 s (3H, Me), 2.72 s (3H, Me). Found, %: C 57.52; H 5.06; N 7.08. $C_{20}H_{20}N_2O_6S$. Calculated, %: C 57.69; H 4.81; N 6.73.

Methyl 5-methoxycarbonylamino-2-phenyl-3-tosylindole-1-carboxylate (IVb) was synthesized as described above for compound **IVa**. Yield 79%, mp 172°C. ^{1}H NMR spectrum, δ, ppm: 8.75 br.s (1H, NH), 8.49 s (1H, 4-H), 8.07 d (1H, H_{arom}, J = 11 Hz), 7.70 d (1H, H_{arom}, J = 11 Hz), 7.55–7.38 m (5H, H_{arom}), 7.32 d (2H, H_{arom}, J = 10 Hz), 7.22 d (2H, H_{arom}, J = 10 Hz), 3.78 s (3H, OMe), 3.68 s (3H, OMe), 2.70 s (3H, Me). Found, %: C 63.07; H 4.41; N 5.80. $C_{25}H_{22}N_2O_6S$. Calculated, %: C 62.76; H 4.60; N 5.68.

The ^{1}H NMR spectra were taken on a Bruker AM-300 spectrometer (300 MHz) in acetone-d_6 using TMS as internal reference. The IR spectra were recorded on an IKS-29 spectrophotometer (4000–400 cm^{-1}) in mineral oil.

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