

## Reaction of *N,N'*-Di(methoxycarbonyl)-*p*-benzoquinonediimine with Meldrum's Acid and its Analogs

A.V. Velikorodov

Astrakhan State University, Astrakhan, 414000 Russia  
e-mail: avelikorodov@mail.ru

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**Abstract**—Reactions of *N,N'*-dimethoxycarbonyl-*p*-benzoquinonediimine in dioxane with 2,2-dimethyl-4,6-dioxo-1,3-dioxane (Meldrum's acid), 2,2-tetramethylene-4,6-dioxo-1,3-dioxane and 2,2-pentamethylene-4,6-dioxo-1,3-dioxane in the presence of MeONa gave rise instead of expectable products of Michael 1,4-addition the corresponding *N,N'*-di(methoxycarbonyl)-*p*-benzoquinonediimines substituted in the ring.

We formerly studied [1, 2] reactions of *N,N'*-di(methoxycarbonyl)-*p*-benzoquinonediimine (**I**) with  $\beta$ -diketones,  $\beta$ -diketoesters, and  $\beta$ -tosyl-substituted carbonyl compounds that depending on the reaction conditions and on the nature of the CH-acid afforded either the corresponding products of Michael addition or indolization products.

At the same time among published data [3, 4] the information on *N,N'*-di(alkoxycarbonyl)-*p*-benzoquinonediimine reactions with polymethylenemalonates, rather strong CH-acids, is practically lacking. For instance, the acidity of 2,2-dimethyl-4,6-dioxo-1,3-dioxane ( $pK_a$  5.1) [5] is comparable to that of dimedone ( $pK_a$  5.2) [6].

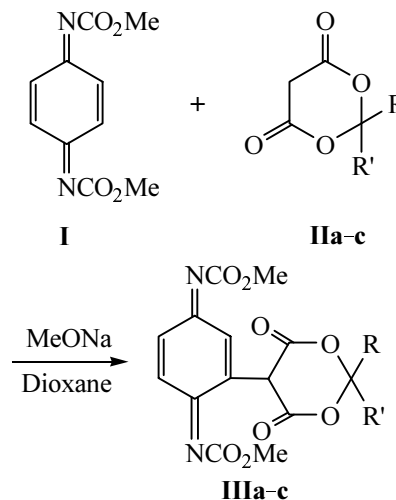
In the present study we investigated reactions of benzoquinonediimine **I** with 2,2-dimethyl-4,6-dioxo-1,3-dioxane (**IIa**), 2,2-tetramethylene-4,6-dioxo-1,3-dioxane (**IIb**), and 2,2-pentamethylene-4,6-dioxo-1,3-dioxane (**IIc**). The process was performed by keeping an equimolar reagents mixture in anhydrous dioxane in the presence of sodium methoxide under TLC monitoring.

Using the data of elemental analysis, IR, and  $^1H$ NMR spectroscopy we established that the reaction products were the respective substituted in the ring *N,N'*-di(methoxycarbonyl)-*p*-benzoquinonediimines (**IIIa–c**) (see table).

Actually, in the IR spectra of compounds **IIIa–c** the absorption bands in the region 3300–3400  $cm^{-1}$  characteristic of stretching vibrations of NH group are lacking, but are present absorption bands at 1620  $cm^{-1}$ , corresponding to the stretching vibrations of C=N group. In the  $^1H$  NMR spectrum signals of aromatic protons are absent but appear signals of quinoid protons in the region 6.65–7.02 ppm

Compounds **IIIa–c** are crystalline substances of cream color melting with decomposition, well soluble in ethyl ether, chloroform, ethanol, and other polar solvents

The probable reaction mechanism may be represented as follows [7]:



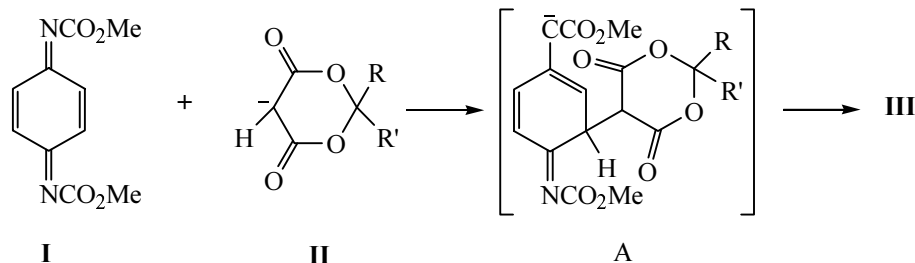
**II, III**, R = R' = Me (**a**); R, R' = (CH<sub>2</sub>)<sub>4</sub> (**b**); R, R' = (CH<sub>2</sub>)<sub>5</sub> (**c**).

The nucleophilic attack of CH-acid on the quinoid ring results in formation of intermediate (A) that is apparently stabilized by hydride ion elimination (see scheme). The validity of this scheme is supported by the lack in the reaction mixture of *p*-di(methoxycarbonyl)benzene [8] that excludes the possibility of compounds **IIIa–c** formation from the products of 1,4-addition by Michael reaction through their oxidation with benzoquinonediimine **I**.

### EXPERIMENTAL

$^1H$  NMR spectra were registered on spectrometer Bruker AC-200 (200.13 MHz) in CDCl<sub>3</sub>, internal refer-

## Scheme.



ence TMS. IR spectra were measured on spectrophotometer IKS-29 in wavenumber range 4000–400  $\text{cm}^{-1}$  from mulls in mineral oil. The purity of compounds obtained was checked by TLC on Silufol UV-254 plates.

Meldrum's acid **IIa** was prepared by procedure from [9].

**2,2-Tetramethylene-4,6-dioxo-1,3-dioxane (IIb).**

At room temperature a mixture of 6.4 g (61.5 mmol) of finely ground malonic acid, 10 ml of freshly distilled acetic anhydride, 0.2 g (1.05 mmol) of *p*-toluenesulfonic acid monohydrate, and 5.5 ml (61.5 mmol) of freshly distilled cyclopentanone was stirred till the malonic acid completely dissolved (for 5 h). The mixture was maintained at 20°C for 170 h, then diluted with water (30 ml), and cooled with ice mixed with sodium chloride. The separated crystalline reaction product was filtered off, washed with water on the filter, dried in air, and crystallized from a mixture petroleum ether–ethanol, 5:2 (by volume). We obtained 6.49 g (62%) of colorless crystalline compound **IIb**, mp 75–76°C. IR spectrum,  $\text{H}$ ,  $\text{cm}^{-1}$ : 1785, 1715 (C=O). Found, %: C 56.24; H 5.99.  $\text{C}_8\text{H}_{10}\text{O}_4$ . Calculated, %: C 56.47; H 5.88.

**2,2-Pentamethylene-4,6-dioxo-1,3-dioxane (IIc)**

was obtained as colorless crystalline compounds by a similar procedure from 3.2 g (30.77 mmol) of malonic acid, 3.2 ml (30.77 mmol) of cyclohexanone, 0.1 g (0.526 mmol) of *p*-toluenesulfonic acid monohydrate, and 5 ml of acetic anhydride. Yield 3.45 g (61%), mp 94–95°C [10].

**Substituted *N,N'*-dimethoxycarbonyl-*p*-benzoquinonediimines (IIIa–c).** To a solution of 1.11 g (5 mmol) of *N,N'*-di(methoxycarbonyl)-*p*-benzoquinonediimine (I) in 5 ml of anhydrous dioxane was added 5 mmol of CH-acid, 0.185 mmol of sodium methoxide, and the mixture was kept at room temperature for 24 h. Then it was poured into 50 ml of petroleum ether, and 1 drop of glacial acetic acid was added. The reaction product was filtered off, dried in air, and crystallized from a mixture chloroform–petroleum ether, 1:5 (by volume).

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Yields, melting points, elemental analyses, IR, and  $^1\text{H}$  NMR spectra of compounds **IIIa–c**

Compd. no.	Yield, %	mp, °C	IR spectrum, $\text{H}$ , $\text{cm}^{-1}$	$^1\text{H}$ NMR spectrum, $\delta$ , ppm	Found, %			Formula	Calculated, %		
					C	H	N		C	H	N
<b>IIIa</b>	52	171	1778, 1725 (C=O), 1620 (C=N), 1535(C=C)	7.02 c (1H), 6.74 d (1H, $J$ 6.4 Hz), 6.68 d (1H, $J$ 6.4 Hz), 4.60 s (1H, SH), 3.89 s (6H, 2OMe), 1.77 s (6H, 2Me)	52.44	4.61	7.48	$\text{C}_{16}\text{H}_{16}\text{N}_2\text{O}_8$	52.75	4.40	7.69
<b>IIIb</b>	61	185	1800, 1720 (C=O), 1620 (C=N), 1535 (C=C)	7.00 c (1H), 6.74 d (1H, $J$ 6.4 Hz), 6.65 d (1H, $J$ 6.4 Hz), 4.62 s (1H, SH), 3.89 s (6H, 2OMe), 1.10–2.00 m (8H)	55.15	4.94	6.98	$\text{C}_{18}\text{H}_{18}\text{N}_2\text{O}_8$	55.39	4.62	7.18
<b>IIIc</b>	59	172	1775, 1725 (C=O), 1620 (C=N), 1530 (C=C)	7.00 c (1H), 6.73 d (1H, $J$ 6.4 Hz), 6.65 d (1H, $J$ 6.4 Hz), 4.64 s (1H, SH), 3.89 s (6H, 2OMe), 1.00–1.95 m (10H)	56.27	5.08	6.78	$\text{C}_{19}\text{H}_{20}\text{N}_2\text{O}_8$	56.44	4.95	6.93

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