Russian Journal of Organic Chemistry, Vol. 39, No. 8, 2003, pp. 1200–1201. Translated from Zhurnal Organicheskoi Khimii, Vol. 39, No. 8, 2003, pp. 1271–1272.

SHORT COMMUNICATIONS

Some Heterocyclization Reactions of *N*,*N*'-Dimethoxycarbonyl-*o*-benzoquinone Diimine

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Received June 13, 2002

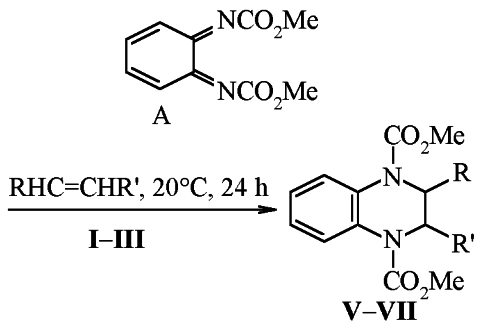
The chemistry of *N*,*N*'-dialkoxy derivatives of *o*-benzoquinone diimine is almost unknown in contrast to that of relatively stable *N*,*N*'-diaroyl and *N*,*N*'-bis(arylsulfonyl) derivatives of the *o*-benzoquinone diimine [1, 2]. We have shown formerly [3] that unlike *N*,*N*'-dimethoxycarbonyl-*p*-benzoquinone diimine [4] the respective ortho-isomer cannot be isolated as an individual compound presumably because it is prone to autocondensation of intermolecular Diels–Alder type [5].

The *ortho*-benzoquinone diimines are known to react as C=C dienophiles [6]. homo- and heterodienes [1, 7]. The capability of 1,4-diaza-1,3-butadiene fragment in the *o*-benzoquinone diimines to play the part of 4π-component in [4+2] and [4+6] cycloadditions is of great interest for the synthesis of azaheterocycles. For instance, *N*,*N*'-diaroyl and *N*,*N*'-diarylsulfonyl derivatives of *o*-benzoquinone diimine react with ordinary, strained, and electron-rich compounds furnishing heterodiene adducts [1, 9].

Here is reported on the results of the study of reactions between *N*,*N*'-dimethoxycarbonyl-*o*-benzoquinone diimine (A) in chloroform *in situ* with 1,3-cyclopentadiene (**I**), cyclhexene (**II**), and styrene (**III**) at 20°C, and also with an ether solution of diazomethane (**IV**) at 0–5°C.

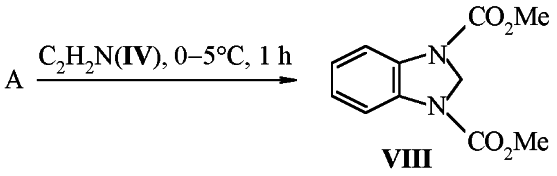
As was revealed by investigation with the use of ^{1}H NMR spectroscopy of reaction products obtained from quinone diimine (A) and compounds **I**–**III** these products resulted from Diels-Alder reaction with reversed electronic requirements and had the structure of the corresponding tetrahydroquinoxaline derivatives **V**–**VII**.

The reaction of *o*-quinone diimine (A) with diazomethane (**IV**) is contrast to the corresponding process involving *N*,*N*'-dimethoxycarbonyl-*p*-benzoquinone diimine [10] is accompanied by liberation of molecular nitrogen and furnishes dihydrobenzimidazole derivative **VIII** whose structure is confirmed by ^{1}H NMR spectrum.



(1)

R,R' = CH=CHCH$_2$ (**V**), (CH$_2$)$_4$ (**VI**); R = Ph, R' = H (**VII**).



To a solution in 25 ml of chloroform of *N*,*N*'-dimethoxycarbonyl-*o*-benzoquinone diimine (**I**) obtained by oxidation of 2.24 g (0.01 mol) of *o*-dimethoxycarboxamido)benzene with 4.43 g (0.01 mol) of lead tetraacetate followed by conventional treatment [4] was added 0.01 mol of compound **I**–**IV**. The solvent was removed, to the residue of compounds **V**–**VII** was added 15 ml of a mixture ether–hexane, 2 : 1. The crystalline reaction products were separated and recrystallized from a mixture chloroform–petroleum ether, 1 : 2. Compound **VIII** precipitated in the course of the reaction; it was separated and recrystallized from ethanol.

Dimethyl 3*a*,9*a*-dihydro-1*H*-cyclopenta[*b*]-quinoxaline-4,9-dicarboxylate (V). Yield 82%, mp 103°C. ^{1}H NMR spectrum, δ, ppm: 2.00–3.20 m

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(2H, CH_2), 3.71 s (6H, 2OMe), 5.51–6.22 m (4H, 4CH), 6.99–7.40 m (4H, H arom). Found, %: C 62.13; H 5.72; N 9.24. $C_{15}H_{16}N_2O_4$. Calculated, %: C 62.50; H 5.56; N 9.72.

Dimethyl 1,2,3,4,4*a*,10*a*-hexahydrophenazine-5,10-dicarboxylate (VI). Yield 79%, mp 199–200°C. ^{1}H NMR spectrum, δ, ppm: 2.00–2.50 m (8H, $4CH_2$), 3.68 s (6H, 2OMe), 5.18–5.45 m (2H, $H^{2,3}$), 6.98–7.40 m (4H, H arom). Found, %: C 62.86; H 6.18; N 9.43. $C_{16}H_{20}N_2O_4$. Calculated, %: C 63.16; H 6.58; N 9.21.

Dimethyl 2,3-dihydro-2-phenylquinoxaline-1,4-dicarboxylate (VII). Yield 59%, mp 132°C. ^{1}H NMR spectrum, δ, ppm: 3.70 s (6H, 2OMe), 3.82 d (2H, CH_2, *J* 6.5 Hz), 5.60 t (1H, H^2, *J* 6.5 Hz), 7.18–7.40 m (9H, H arom).

Dimethyl 2,3-dihydrobenzimidazole-1,3-dicarboxylate (VIII). Yield 87%, mp 181–182°C. ^{1}H NMR spectrum, δ, ppm: 1.51 s (2H, CH_2), 3.78 s (6H, 2OMe), 7.02–7.38 m (4H, H arom).

^{1}H NMR spectra were recorded on spectrometer Bruker AC-200 (200.13 MHz) in acetone-d_6, internal reference TMS.

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