ISSN 1070-4280, Russian Journal of Organic Chemistry, 2007, Vol. 43, No. 6, pp. 861–863. © Pleiades Publishing, Ltd., 2007.
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Synthesis of 3-(2-Oxo-2,3-dihydrobenzo[*b*]furan-3-ylidenehydrazono)-2,3-dihydrobenzo[*b*]furan-2-one

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Received April 4, 2006

Abstract—Reactions of benzophenone and fluoren-9-one hydrazones with (2-hydroxyphenyl)oxoacetic acid gave [carboxy(2-hydroxyphenyl)methylidenehydrazono](2-hydroxyphenyl)acetic acid which underwent intramolecular cyclization with formation of 3-(2-oxo-2,3-dihydrobenzo[*b*]furan-3-ylidenehydrazono)-2,3-dihydrobenzo[*b*]furan-2-one. The symmetric azine was also obtained by reactions of (2-hydroxyphenyl)oxoacetic acid with triphenylphosphoranylidenehydrazones derived from benzophenones, fluoren-9-one, and 1-methyl-2,3-dihydro-1*H*-indole-2,3-dione.

DOI: 10.1134/S1070428007060103

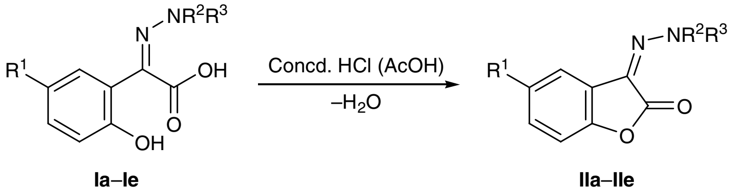
The synthesis of hydrazono(2-hydroxyphenyl)acetic acids **Ia**–**Ie** and their cyclization into 3-hydrazono-2,3-dihydrobenzo[*b*]furan-2-ones **IIa**–**IIe** on heating in glacial acetic acid or concentrated hydrochloric acid (Scheme 1) were described in [1–3]. Since early 1970s these transformations remained beyond the scope of researchers' interest. Taking into account that compounds **I** and **II** may be important from the preparative viewpoint [4], we performed a study in this field.

We found that reactions of (2-hydroxyphenyl)oxoacetic acid (**III**) with benzophenone and fluoren-9-one hydrazones (reactant ratio 1 : 1 or 2 : 1) in anhydrous toluene at 20–25°C give no expected compounds **I**. Instead, the products are (2-hydroxyphenyl)[carboxy(2-hydroxyphenyl)methylidenehydrazono]acetic acid (**IV**, yield 67–72%) and azines **Va**–**Vd** (Scheme 2). Compounds **Va**–**Vd** were described in [5–7].

The IR spectrum of **IV** contained a broadened absorption band at 1744 cm^{-1} due to stretching vibrations of the acid carbonyl group and bands in the region 1617–1599 cm^{-1}, belonging to C=N and C=C bonds. Compound **IV** displayed in the ^{1}H NMR spectrum a multiplet centered at δ 7.20 ppm from aromatic protons and a broadened signal at δ 11.00 ppm from the acid OH protons. In the mass spectrum of **IV**, the molecular ion peak (*m*/*z* 328) had a relative intensity of 1.9%, and fragment ion peaks did not contradict the assumed structure.

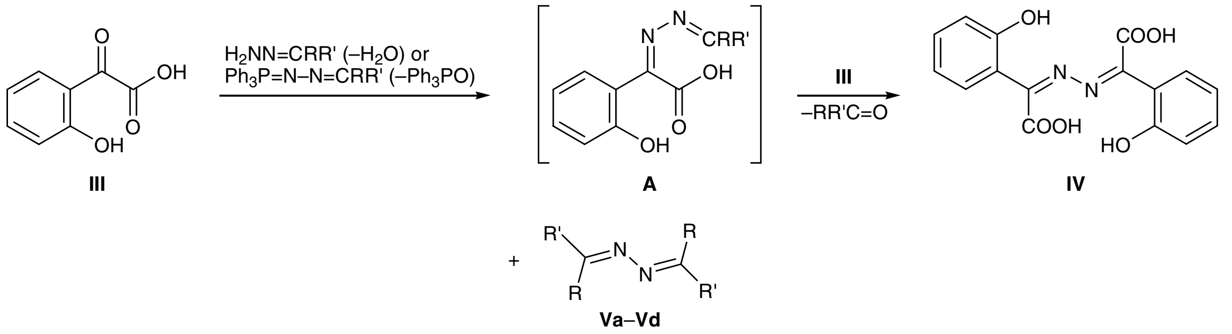
Presumably, the reaction includes intermediate formation of unsymmetrical azine like **A**, which reacts with the second molecule of acid **III** to produce azine **IV**. This reaction path is confirmed by the presence of the corresponding ketones (benzophenones or fluoren-9-one) in the reaction mixture. Acid **III** also reacted under analogous conditions with triphenylphosphoranylidenehydrazones derived from benzophenones, fluoren-9-one, and 1-methyl-2,3-dihydro-1*H*-indole-2,3-dione to give azine **IV**, but the yield of

Scheme 1.

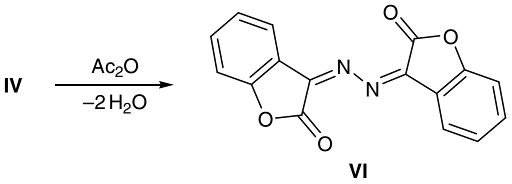


$R^1 = R^2 = H$, $R^3 = Ph$ (**a**), $NH_2C(O)$ (**b**), $NH_2S(O)$ (**c**); $R^1 = Me$, $R^2 = H$, $R^3 = Ph$ (**d**), PhC(O) (**e**).

Scheme 2.



V, R = R′ = Ph (**a**), R = Ph, R′ = 4-BrC_6H_4 (**b**); RR′ = 9*H*-fluoren-9-ylidene (**c**), 1-methyl-2-oxo-2,3-dihydro-1*H*-indol-3-ylidene (**d**).



the latter was considerably smaller. Apart from triphenylphosphine oxide, the corresponding symmetric azines **Va**–**Vd** were isolated from the reaction mixture. Here, as in the above reaction, compound **IV** is likely to be formed through intermediate **A**. Thus, the processes leading to symmetric azines **IV** and **V** are concurrent, and the product ratio is determined most probably by thermodynamic factors.

On heating in acetic anhydride, compound **IV** underwent intramolecular cyclization to 3-(2-oxo-2,3-dihydrobenzo[*b*]furan-3-ylidenehydrazono)-2,3-dihydrobenzo[*b*]furan-2-one (**VI**). The IR spectrum of **VI** contained an absorption band at 1812 cm^{-1} due to the lactone carbonyl groups, and C=N and C=C vibrations appeared in the region 1609–1598 cm^{-1}. The aromatic protons gave a four-proton multiplet centered at δ 7.30 ppm and two two-proton multiplets at δ 7.65 and 7.83 ppm. No molecular ion peak was present in the mass spectrum of **VI**, but the fragment ion peaks (see Experimental) were consistent with its structure.

EXPERIMENTAL

The IR spectra were recorded in mineral oil on FSM-1201 and Specord M80 instruments. The ^1H NMR spectra were measured on RYa-2310 (60 MHz) and Bruker DRX-500 (500 MHz) spectrometers from solutions in DMSO-d_6 relative to TMS as internal reference. The mass spectra (electron impact, 70 eV) were obtained on a Varian MAT-311 instrument with direct sample admission into the ion source. The progress of reactions and the purity of products were monitored by TLC on Silufol UV-254 plates (diethyl ether–benzene–acetone, 10:9:1).

[Carboxy(2-hydroxyphenyl)methylidenehydrazono](2-hydroxyphenyl)acetic acid (IV). *a.* A suspension of 0.01 mol of benzophenone or fluoren-9-one hydrazone in 10 ml of anhydrous toluene was added to a solution of 1.66 g (0.01 mol) of acid **III** in 10 ml of the same solvent, and the mixture was stirred at room temperature until it became homogeneous. The resulting solution was cooled to 0°C, and the precipitate was filtered off and recrystallized from toluene. Yield 67–72%, yellow crystals, mp 183–185°C (decomp.). Mass spectrum, *m*/*z* (I_{rel}, %): 310 (2.4), 292 (22.6), 264 (12.3), 238 (15.5), 192 (20.1), 164 (5.7), 146 (7.3), 120 (43.6), 102 (100), 93 (28.6), 76 (21.4). Found, %: C 58.82; H 3.58; N 8.60. $C_{16}H_{12}N_2O_6$. Calculated, %: C 58.54; H 3.66; N 8.54.

b. A suspension of 0.01 mol of benzophenone or fluoren-9-one triphenylphosphoranylidenehydrazone in 10 ml of anhydrous toluene was added to a solution of 1.66 g (0.01 mol) of acid **III** in 10 ml of the same solvent, and the mixture was stirred for 24 h at room temperature. The mixture was cooled to 0°C, and the precipitate was filtered off and recrystallized from toluene. Yield 42–58%.

3-(2-Oxo-2,3-dihydrobenzo[*b*]furan-3-ylidenehydrazono)-2,3-dihydrobenzo[*b*]furan-2-one (VI). A mixture of 3.28 g (0.01 mol) of compound **IV** and 20 ml of acetic anhydride was kept at room temperature until it became homogeneous. It was then cooled to 0°C, and the precipitate was filtered off and recrystallized from acetonitrile. Yield 2.59 g (89%), orange crystals, mp 265–267°C (decomp.). Mass spectrum, *m*/*z* (I_{rel}, %): 264 (63.8), 236 (100), 208 (20.5), 102 (5.9), 76 (11.3). Found, %: C 65.68; H 2.78; N 9.55. $C_{16}H_8N_2O_4$. Calculated, %: C 65.75; H 2.74; N 9.59.

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