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LETTERS TO THE EDITOR

BENZOYLACETYLATION OF ALLOBETULIN AND ALLOBETULONE OXIME BY BENZOYLKETENE GENERATED *in situ* DURING THERMOLYSIS OF 5-PHENYL-2,3-DIHYDROFURAN-2,3-DIONE

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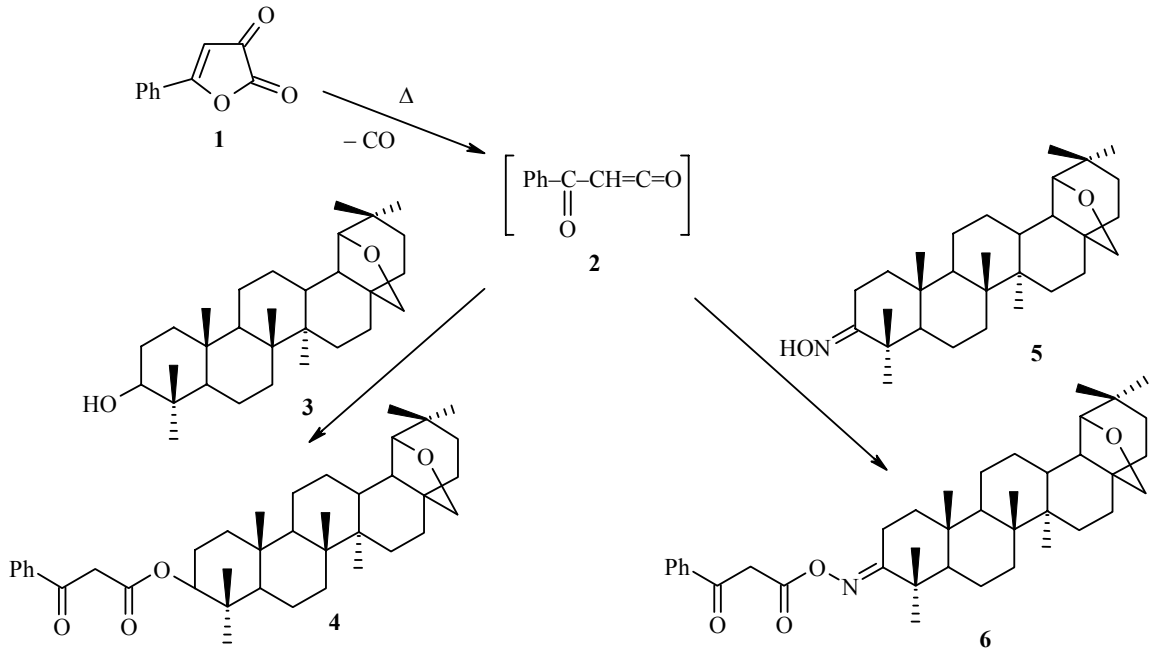
Primary and secondary alcohols open up the ring of 5-aryl-2,3-dihydrofuran-2,3-diones at room temperature to form the corresponding aroylpyruvic acid esters [1]. In contrast to the indicated alcohols, allobetulin (**3**) reacts with 5-phenyl-2,3-dihydrofuran-2,3-dione (**1**) at 110°C and forms the corresponding O-benzoylacetic acid **4**. Its formation is probably connected with intermediate generation of benzoylketene **2**, which benzoylacetylates the hydroxyl group of allobetulin.



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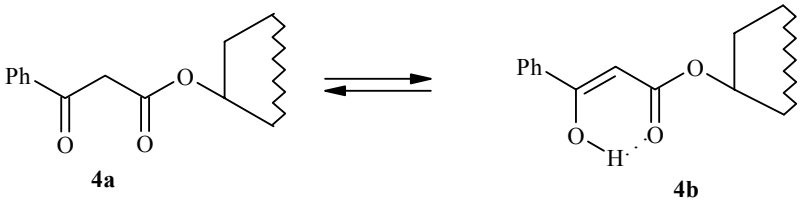
Such an unusual reaction most likely is connected with the presence of a bulky polycyclic substituent in reagent **3**, hindering nucleophilic addition of the hydroxyl group at the α-carbonyl of furandione **1**, which rules out opening of the heterocycle at the $O–C_{(2)}$ bond [2]. In deuterochloroform solution, compound **4** exists both in the keto form **4a** and in the enol form **4b**. The keto to enol ratio is 9:1.



4a **4b**

Allobetulone oxime (**5**) reacts with furandione **1** under similar conditions. In this case, the reaction product is allobetulone oxime O-benzoylacetate (**6**). The reaction of furandione **1** with oxime **5** can occur simultaneously in two directions: with generation of benzoylketene followed by benzoylacetylation of the oxime group of the reagent; with intermediate formation of the allobetulone oxime O-benzoylpyruvate, undergoing decarbonylation under the reaction conditions to form O-benzoylacetate **6** [3]. 100% of this compound is found in the keto form.

The IR spectra were recorded on a UR-20 in nujol, the ^1H NMR spectra were recorded on a MERCURYplus 300 (300 MHz) in $CDCl_3$, internal standard HMDS (δ 0.05 ppm).

Allobetulin O-Benzoylacetate (4). A solution of compound **1** (0.68 mmol) and compound **3** (0.68 mmol) was refluxed for 30 min in anhydrous toluene (30 ml). The solvent was distilled off, the residue was recrystallized from DMSO; mp 234-236°C, yield 61%. IR spectrum, ν, cm^{-1}, 1710 (ether C=O, weak), 1670 (ketone C=O,). ^1H NMR spectrum, δ, ppm: 0.64-3.70 (49H, set of signals from aliphatic protons); 3.92 (2H, s, $COCH_2CO$); 5.60 (1H, s, =CH–); 7.32-7.89 (5H, m, C_6H_5); 12.61 (1H, s, OH). Found, %: C 79.5; H 9.4. $C_{39}H_{56}O_4$. Calculated, %: C 79.6; H 9.5.

Allobetulone Oxime O-Benzoylacetate (6). A solution of compound **1** (0.9 mmol) and compound **5** (0.9 mmol) was refluxed for 30 min in anhydrous toluene (30 ml). The solvent was distilled off, the residue was recrystallized from a 10:1 ethanol–chloroform mixture; mp 245-246°C, yield 70%. IR spectrum, ν, cm^{-1}: 1740 (ether C=O, weak), 1660 (ketone C=O). ^1H NMR spectrum, δ, ppm: 0.73-3.72 (48H, set of signals from aliphatic protons); 4.13 (2H, s, $COCH_2CO$); 7.27-7.92 (5H, m, C_6H_5). Found, %: C 77.7; H 9.1; N 2.2. $C_{39}H_{55}NO_4$. Calculated, %: C 77.9; H 9.2; N 2.3.

REFERENCES

1. Yu. S. Andreichikov, S. P. Tendryakova, Yu. A. Nalimova, and G. D. Plakhina, *Khim. Geterotsikl. Soedin.*, 1030 (1977).
2. Yu. S. Andreichikov, Yu. A. Nalimova, M. I. Vakhrin, S. P. Tendryakova, and A. P. Kozlov, *Khim. Geterotsikl. Soedin.*, 744 (1982).
3. D. D. Nekrasov, V. G. Chizh, Yu. S. Andreichikov, and R. R. Makhmudov, *Khim.-Farm. Zh.*, **28**, 30 (1994).